CATALYTIC HYDROFORMYLATION OF ALKENES AND POLYALKENES: NOVEL APPROACHES TO CATALYST SYNTHESIS, CHARACTERIZATION AND RECYCLING

BY

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TO

MY WIFE

& CHILDREN

ACKNOWLEDGMENT

Praise be to Allah Almighty, The all Knowing. Blessing and peace be upon our leader Muhammad, his family, his companions, and those that follow his guidance until the last day.

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DISSERTATION ABSTRACT

NAME OF STUDENT: JIMOH TIJANI

TITLE OF STUDY: CATALYTIC HYDROFORMYLATION OF ALKENES AND POLYALKENES: NOVEL APPROACHES TO CATALYST SYNTHESIS, CHARACTERIZATION AND RECYCLING

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Hydroformylation of olefins is a versatile method and well-established industrial process for the production of aldehydes using transition metal complexes as homogeneous catalysts. Currently, worldwide production of aldehydes exceeded seven million tons/year. Rhodium (I) complexes are the most active and selective catalysts for hydroformylation reaction. For any industrial application of homogeneously catalyzed reaction, a complete recycling of the generally expensive catalyst should be guaranteed. A thermomorphic system is characterized by solvent pairs that reversibly changes from biphasic to monophasic and vice versa as a function of temperature. We have applied the thermomorphic approach to rhodium-catalyzed hydroformylation of higher olefins (C>6). The effect of CO/H_2 pressure, ligand/catalyst ratio on activity, selectivity and recycling were studied on 1-octene and other olefins.

The impregnation of $HRhCO(PPh_3)_3$ on mesoporous materials such as MCM-41, through Phosphotungstic acid (PTA) gives a novel hydroformylation catalyst, which was characterized by XRD, IR, and ^{31}P CP MAS NMR. The activity, selectivity and recycling of this supported catalyst were established by hydroformylation of 1-octene. The catalyst activity was shown by the recycling capability for several times without significant loss of activity.

Results are presented on a novel application of catalysis to chemical modification of commercially available polybutadiene polymers. The functionalized polyaldehyde products are key intermediates in the development of various polymer derivatives which form the basis for various novel material and component applications, such as manufacture of automobile body components by reaction injection molding processing. Characterization of the reaction products using ^{13}C and ^{1}H NMR shows that the olefin units in the polybutadiene are selectively hydroformylated to the 1,2-terminal branched and 1,4-internal branched aldehydes products.

DOCTOR OF PHILOSOPHY DEGREE

KING FAHD UNIVESITY OF PETROLEUM & MINERALS

DHAHRAN SAUDI ARABIA

الخلاصة

الاســـــــــــم: **جيـــمـــو تيـــجانـــي**

عنوان الرسالة: **الهيدروفورميلاشن بالتحفيز للألكينات وعديدات الألكينات : طريقة فريدة لتصنيع المحفز وتشخيصه واعادة استخدامه .**

التخصـــــــص: **الكيـــمـــيـــاء**

تاريخ التخـرج: **مايـــــو -2006**

ان عملية الهيدروفورميلاشن للألكينات لهي طريقة متعددة الاستخدامات ومعروفة بشكل جيد صناعيا في عملية انتاج الالدهيدات باستخدام معقدات المعادن الانتقالية كمحفز متجانس. ان الانتاج العالمي حاليا من الالدهيدات يفوق السبع ملايين طن سنويا. ان معقدات الروديوم (I) هي الافضل كفاءة وانتقائية لتفاعل الهيدروفورميلاشن.
انه من المهم لاي عملية صناعية تستخدم تفاعلات المحفزات المتجانسة ان يكون هناك ضمان لعملية اعادة استخدام المحفز(recycling) المكلف ماديا. ان نظام ال(thermomorphic) مميز باستخدام زوجين من المذيبات واللتي تتبادل بشكل عكسي (reversible) من الحالة الثنائية (biphasic) الى الحالة الاحادية (monophasic) وبالعكس وذلك اعتمادا على درجة الحرارة. ولقد تم استخدام طريقة ال(thermomorphic) لتفاعلات الهيدروفورميلاشن المحفزة بالروديوم وذلك للالكينات العالية(C>6). ولقد تمت دراست تأثير تغيير نسبة ضغط (CO/H_2) و (ligand/catalyst) على الكفاءة والانتقائية واعادة الاستخدام للمركب 1-أوكتين وغيره من الألكينات.
ان عملية (impregnation of $HRhCO(PPh_3)_3$) على مادة (mesoporous materials MCM-41) باستخدام (Phosphotungstic acid (PTA)) قد أعطت نتائج فريدة لمحفز الهيدروفورميلاشن واللتي تم فحصها باستخدام (XRD, IR, and ^{31}P CP MAS NMR). ولقد تم تأسيس الكفاءة والانتقائية واعادة الاستخدام لهذا المحفز المدعم بواسطة الهيدروفورميلاشن لمركب 1-أوكتين. ولقد تم فحص كفاءة المحفز عن طريق القدرة على اعادة الاستخدام ولعدة مرات بدون اي فقدان يذكر للكفاءة.
لقد تم استخدام النتائج على التطبيق الفريد لتحفيز التعديل الكيميائي لمبلمرات عديد البيوتادايين المتوفر صناعيا. ان منتجات عديدات الألدهيدات الحاملة للمجموعات المختلفة واللتي تشكل مركبات وسيطة هامة لتطوير مختلف مشتقات المبلمرات واللتي بدورها تشكل أساسا لمختلف المواد الفريدة الهامة لتطبيقات عديدة منها صناعة مكونات أجسام السيارات باستخدام تقنية عملية الحقن بالقوالب. ولقد أظهرت عملية فحص نواتج التفاعل باستخدام (^{13}C and ^{1}H NMR) أن وحدات الألكين في عديد البيوتادايين قد تمت لها عملية الهيدروفورميلاشن لتعطي نواتج الألدهيدات (1,2-terminal branched and 1,4-internal branched).

درجة الدكتوراة في الفلسفة

جامعة الملك فهد للبترول و المعادن

الظهران-المملكة العربية السعودية

CHAPTER 1

1.0 INTRODUCTION AND LITERATURE OVERVIEW

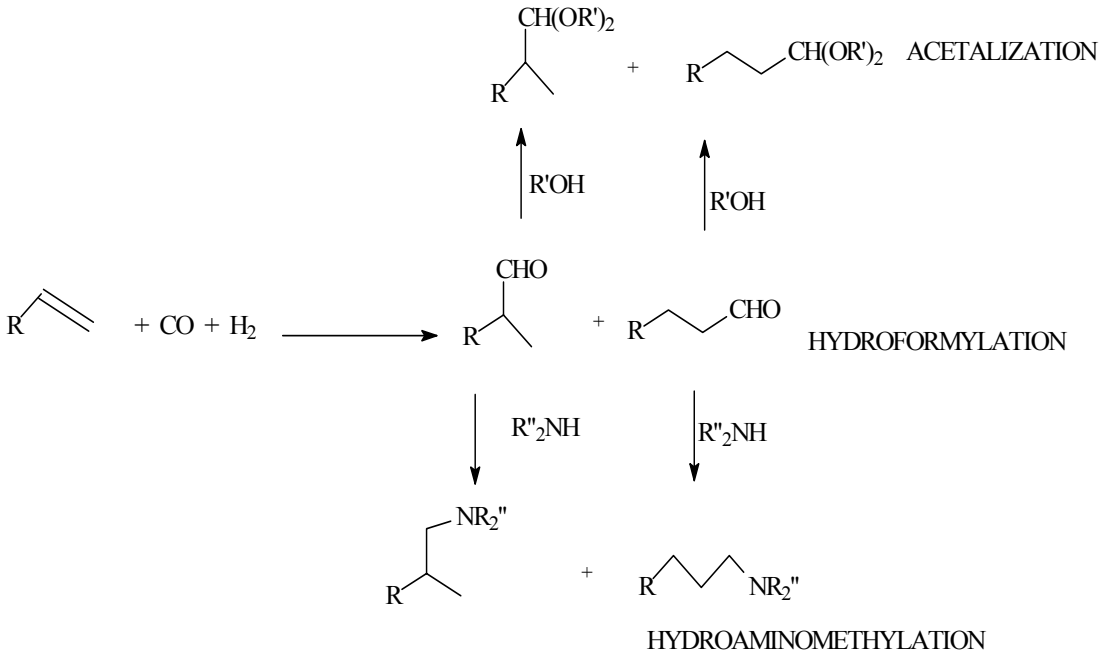
1.1 Introduction to hydroformylation

The term “carbonylation” was coined by W. Reppe during the thirties and is generally used to refer to those reactions in which CO alone or CO combined with other compounds (especially nucleophiles with mobile H-atom) are introduced into particular substrates (saturated or unsaturated) (1). "Carbonylation" is used here as a generic term, including reactions such as formylation, hydroformylation, and hydrocarboxylation, which involve the introduction of a carbonyl group into an organic substrate. Group VIIIB metals, especially Fe, Co, Ni, Ir, Rh, Ru, Os, Pt, and Pd in the form of metal carbonyls or other derivatives that are transformed into carbonyls under reaction conditions, catalyze these reactions (1,2).

Carbonylation reactions rank among the most useful transformations homogeneously catalyzed by transition-metal complexes, forming the basis for industrial and laboratory processes currently in practice (3). Some of the initial scientific discoveries in this field gradually evolved into large-scale commercial carbonylation processes. Noteworthy among the commercial carbonylation processes are the ‘oxo’ process (olefin hydroformylation), the Reppe process (hydrocarboxylation of acetylene into acrylic acid) and Monsanto process (carbonylation of methanol into acetic acid) (3-5). These processes are employed worldwide to prepare millions of tons of commodity chemicals each year. In addition, it has been predicted that the importance of carbonylation reactions in the total chemical output will continue to grow as several new carbonylation processes are

expected to reach commercialization soon. The basic reason is that the feedstock i.e. syngas (carbon monoxide & hydrogen) is versatile and inexpensive (5).

Hydroformylation reaction is a special type of carbonylation, where hydrogen and formal group "CHO" are added across an unsaturated bond to give aldehydes (1). When alkenes are hydroformylated in the presence of alcohols, dialkoxyacetals are formed and this reaction is known as acetalization. Similarly, the consecutive reaction of hydroformylation, amination and reduction is known as hydroaminomethylation (Scheme 1.1) (6).



Scheme 1.1

1.2 BACKGROUND ON HYDROFORMYLATION

Hydroformylation was discovered by Otto Roelen in 1938 during an investigation of the origin of oxygenated products occurring in cobalt catalyzed Fischer-Tropsch reactions. Roelen's observation was that ethylene, H_2 and CO were converted into propanal, which marked the beginning of hydroformylation catalysis (Eq. 1.1). Both linear

and branched products can be produced, although the linear aldehydes are usually the more desirable products. Depending on the catalyst and conditions, the aldehydes can be directly reduced to alcohols during the reaction (1,2,6).

$$CH_2{=}CH_2 + CO + H_2 \xrightarrow{[Co]} CH_3CH_2\overset{\overset{O}{\|}}{C}H \qquad \text{Eq. 1.1}$$

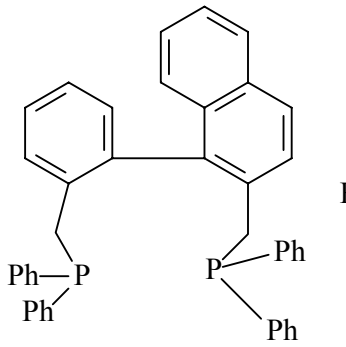
Cobalt catalysts completely dominated the industrial hydroformylation until the early 1970's when rhodium catalysts were commercialized (7). In 1992, ~70% of all hydroformylation processes were based on rhodium triarylphosphine catalysts, which excel with C_8 or lower alkenes and where the high regioselectivity to linear aldehydes is critical (8). In 1965 Osborn, Young and Wilkinson reported that Rh (I)-PPh_3 complexes were active and highly selective as hydroformylation catalysts of 1-alkenes, even at ambient conditions (9-11). Although Slough and Mullineaux had submitted a patent in 1961 claiming the Rh/phosphine combinations for hydroformylation catalysis, it was Wilkinson's work that really ignited the serious interest in rhodium phosphine hydroformylation catalysts. The initial catalyst system was derived from Wilkinson's catalyst, $RhCl(PPh_3)_3$, but it was rapidly discovered that halides were inhibitors of the hydroformylation. It was best, therefore, to start with rhodium complexes that contain no halides. $HRh(CO)(PPh_3)_3$ and $Rh(acac)(CO)_2$ (acac = acetylacetonate) are two commonly used starting materials for hydroformylation (10-12). Wilkinson noted that $HRh(CO)(PPh_3)_3$ was very selective towards aldehyde products (no alcohol formation, no alkene hydrogenation or isomerization) and that a very high ratio of linear to branched aldehyde (20:1) for a variety of 1-alkenes could be obtained under ambient conditions (25° C, 1 bar 1:1 H_2/CO). At higher temperatures, the rate increased, but the

regioselectivity dropped (9:1 at 50° C). At 80-100 bars of H_2/CO, the ratio of the linear to branched aldehyde decreased to only 3:1 (13). Pruett (at Union Carbide) quickly provided the next critical discovery that, along with the work of Booth and coworkers at Union Oil, allowed commercialization of the $HRh(CO)(PPh_3)_3$ technology. They found that the use of rhodium with excess phosphine ligand created an active, selective, and stable catalyst system at 80-100 psi and 90°C (14). Union Carbide, in conjunction with Davy Powergas and Johnson Matthey, subsequently developed the first commercial hydroformylation process using rhodium and excess PPh_3 in the early 1970's. The need for excess phosphine arises from the facile Rh-PPh_3 dissociation equilibrium, loss of PPh_3 from $HRh(CO)(PPh_3)_3$ generates considerably more active but less regioselective hydroformylation catalysts. The addition of excess phosphine ligand shifts the phosphine dissociation equilibrium back towards the more selective $HRh(CO)(PPh_3)_3$ catalyst. This explains why higher CO partial pressures lower the product regioselectivity, in marked contrast to what is observed for $HCo(CO)_4$-catalyzed hydroformylation (15).

The electronic and steric properties of the phosphine ligand(s) can have dramatic effects on the rate and selectivity of the rhodium catalysts. Electron-rich alkylated phosphines generally have a negative effect on the rate and the regioselectivity of the reaction, while more electron deficient phosphines such as PPh_3 and phosphites generate more active and selective catalysts (16).

Union Carbide and Eastman Kodak have independently developed a new generation of chelating bisphosphine rhodium catalysts that show remarkably high product regioselectivities and good to high activities. Interestingly, the two chelating bis-phosphine ligand systems are structurally related (17). The best Eastman Kodak bisphosphine ligand system, developed by Devon, Phillips, Puckette and coworkers at

Texas Eastman is called BISBI* and forms a chelate to the rhodium center. This catalyst is highly selective, giving linear to branched aldehyde product ratio in the hydroformylation of propylene of > 30:1 (commercial Rh/PPh_3 catalysts give a ratio of linear to branched aldehyde around 8:1) with rates similar to or moderately faster than Rh/PPh_3 (17).



BISBI* (I)

1.3 OVERVIEW OF THE EXISTING RECYCLING CONCEPTS

The recycling concepts can be divided into four main classes. An overview of these recycling concepts is given in Figure 1.1. Using the concept of thermal and chemical stability, the products are separated by distillation or by precipitation of the catalyst. This concept is applied in the Wacker-Hoechst process (palladium/copper-catalyzed oxidation of ethylene to acetaldehyde) and in the Monsanto/Cativa process: the products-acetaldehydes and acetic acid- are low-boiling products which can be separated by an easy distillation: then the distillation residue which contains the catalyst can be recycled (18,19).

The method of immobilization of homogeneous catalyst on a solid or liquid support [supported liquid-phase catalysis (SLPC) or supported aqueous-phase catalysis (SAPC)] or by the membrane processes is not applied in the chemical industry. The yields and selectivities are lower than the "classical" homogenously catalyzed reaction, and also

the related problems, such as bleeding (leaching), add a complication to the technical realization.

The last and very popular recycling method includes the concept of multiphase systems that contains other subgroups. The phase transfer catalysis (PTC) and the thermo-regulated phase-transfer catalysis (TRPTC) are not applied in chemical industry, too. The special ligands used in the TRPTC act as surfactants (e.g., nonionic water-soluble phosphines with polyoxyethylene moieties). With the increase of the temperature, such ligand and therefore the whole complex will "change" its solubility from the aqueous to the organic phase at a special temperature ("cloud point"), which means that the complex has an inverse solubility above this point (20-23).

The most popular subgroup of the concept of multiphase systems is the liquid/liquid two phase technique (LLTP) which is, e.g., used in the SHOP process as well as in the Ruhrchemie /Rhone-Poulenc's (RC/RP) process and has decisively contributed to the boom in homogeneous catalysis (18,19,24). In this process, the catalyst is dissolved in polar, mostly aqueous solvent, which is not miscible with the products. After the reaction, the two phases can be separated by simple decantation. Another subgroup of LLTP is the thermomorphic biphasic catalysis (TMBC). In the TMBC, the reaction is carried out in a single phase by repression of the miscibility gab at reaction temperature, decreasing the temperature to room temperature a separation in two phases takes place and an easy catalyst/product separation is possible (25).

1.3.1 WATER-SOLUBLE LIGANDS

Over the past two decades, an increasing interest has been focused on the chemistry of water-soluble transition metal complexes and two-phase catalysis (16,17).

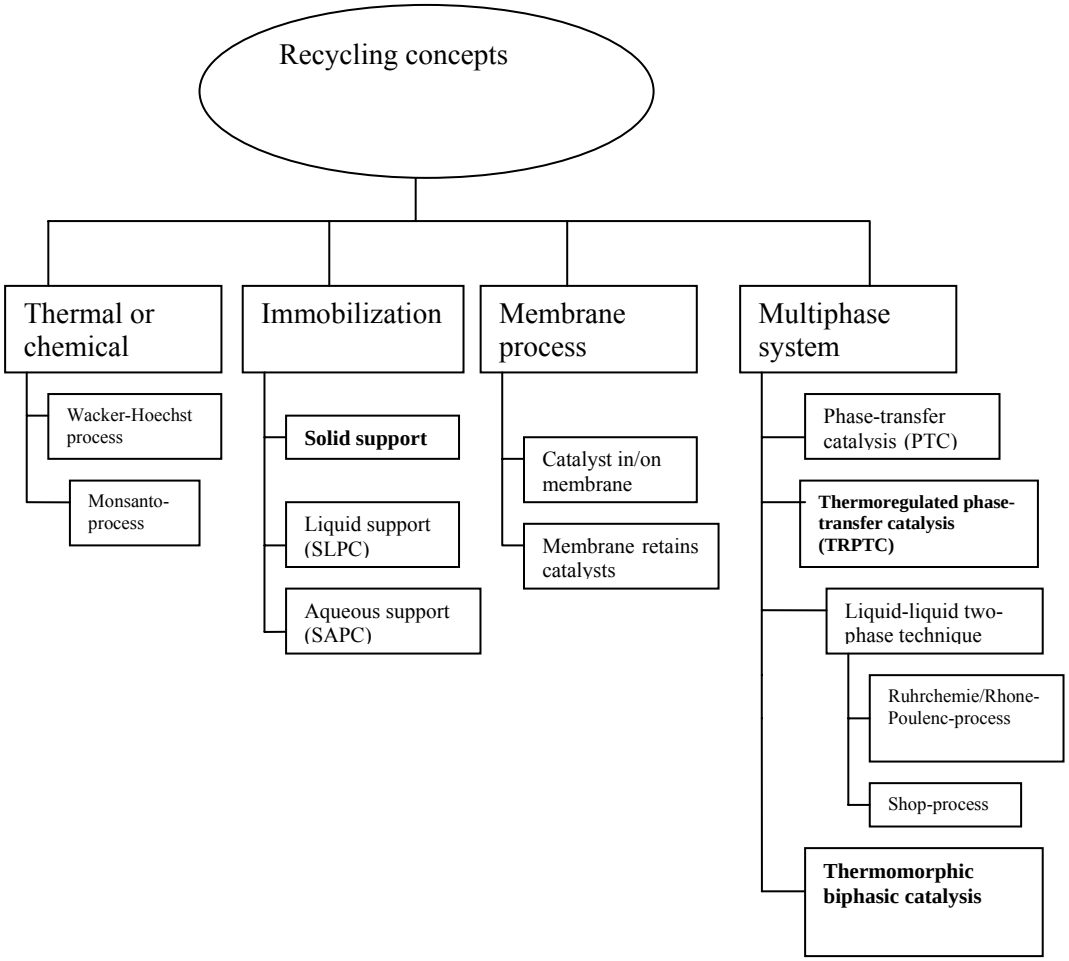

Recycling concepts
Thermal or chemical
Wacker-Hoechst process
Monsanto-process
Immobilization
Solid support
Liquid support (SLPC)
Aqueous support (SAPC)
Membrane process
Catalyst in/on membrane
Membrane retains catalysts
Multiphase system
Phase-transfer catalysis (PTC)
Thermoregulated phase-transfer catalysis (TRPTC)
Liquid-liquid two-phase technique
Ruhrchemie/Rhone-Poulenc-process
Shop-process
Thermomorphic biphasic catalysis

Figure 1.1

One reason for this interest is the stimulating introduction of triphenylphosphine trisulfonate (TPPTS) and aqueous/organic two-phase systems to the rhodium-catalyzed hydroformylation of propene (Ruhrchemie /Rhone-Poulenc's process in 1984) (26). However, the use of water as a second phase has indeed its limitations, especially when the water-solubility of the organic substrates proves too low, preventing adequate transfer of the organic substrate into the aqueous phase or at the phase boundary and consequently reducing the reaction rates. This problem can be solved by introducing a surfactant (or using ligand that confer surfactant properties) or by adding a solvating agent or perhaps using a co-solvent (27). Those measures increase either the mutual solubility of the components or the mobility across the phase boundaries. However, from an engineering and economic standpoint, it is also important to remember that any 'foreign additive' will increase the difficulty and the cost of the purification step (27).

Chaudhari et al. (28) were the first to suggest the introduction of 'promoter ligands' that are soluble exclusively in organic phase, thus modifying the solubility of the complex internally. By adding triphenylphosphine (TPP), which is soluble in organic solvents, to a rhodium complex containing the water-soluble ligand TPPTS, they increase the rate of the hydroformylation of the extremely water-insoluble 1-octene by a factor of 10-50. During the reaction a ligand exchange leads to the formation of mixed-ligand complexes of the type $[RhH(CO)(TPPTS)_{3-x}(TPP)_x]$, which contain the two types of ligands, ligands soluble in organic solvents (TPP) and water-soluble ligands (TPPTS).

1.3.2 THERMOREGULATED PHASE TRANSFER CATALYSIS

The problem of 'foreign additive' is avoided in an approach discovered by Bergbreiter et al. (29). They applied the designation 'smart ligand' in describing the

derivatives of polyethylene oxide, which are known to have inverse temperature dependence in water. The end groups of these polymers were chemically modified to yield phosphine ligands that are soluble at low temperatures which is a phase-separate mixture at higher temperatures i.e. has an inverse temperature-dependent solubility in water.

$$HO\text{-}(CH_2CH_2O)_n\text{-}H \xrightarrow[Et_3N,\ CH_2Cl_2]{CH_3SO_2Cl} CH_3SO_2O\text{-}(CH_2CH_2O)_n\text{-}SO_2CH_3 \xrightarrow{LiPPh_2}$$

$$Ph_2P\text{-}(CH_2CH_2O)_{n-1}CH_2CH_2\text{-}PPh_2 \qquad (II)$$

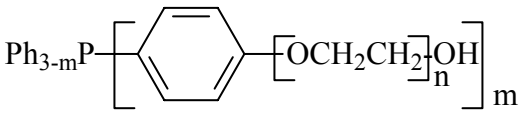
Scheme 1.2

Cationic Rh(I) complexes prepared using ligands derived from II have an inverse temperature-dependent solubility and a lower critical solution temperature (LCST) like the starting ligand. RhCl(ligand II)$_{1.5}$ was tested in a catalytic hydrogenation of allyl alcohol in water. The reaction proceeded at a rate of 2 mmol of H_2/mmol Rh/h at 0^{o}C. On heating the sample to 40-50^{o}C, the reaction stops, although the normal Arrhenius-type kinetics suggest that this temperature should lead to a rate 20-fold faster. This change in rate is due to solubility changes that the complex experienced on heating. This effect is reversed on cooling to 0^{o}C where the ligand is re-hydrated and dissolved, and up to four heating/cooling cycles have been observed (29).

Thermoregulated phase transfer catalysis (TRPTS) proposed by Jin and co-workers (21) provides a perspective future in a path to aqueous/organic biphasic hydroformylation of water-immiscible olefins. Jin and co-workers studied the properties of poly(ethylene oxide)-substituted triphenylphosphines (PEOTPPs) (III) and found that the PEOTPPs are completely soluble in water when (N = m.n) $\geq$ 8. Furthermore, their solubility in water can be controlled by varying the chain length. With their poly(ethylene

oxide)-chains, the PEOTPPs possess, as expected, the property of the inverse temperature-dependent solubility in water with a cloud point (determined in 3 wt% of ligand in water) which range from 26-95^{o}C. On the other hand, the solubility of the poly(ether)-substituted compounds in some non polar aprotic solvents, such as toluene and heptane, increases with the increase of the temperature (21).

The two properties described above enable transition metal complexes containing the poly(ethylene oxide)-substituted ligands to act as water-soluble catalysts that possess a thermoregulated phase-transfer function in the aqueous/organic two-phase system. The reaction is conducted as shown in Figure 1.2.



(III)

m = 1, 2, or 3; N = m.n = 8-25

At the starting point, the catalyst resides in the aqueous phase and the substrate in the organic phase. By heating above the cloud point (temperature above which the complex is not soluble in water) of the complex, the catalyst is transferred into the organic phase to catalyze the reaction. At end of the reaction, the mixture is cool to room temperature, and the catalyst returns to the aqueous phase and the product remains in the organic phase. This makes the separation easy and efficient.

A novel polyalkyl glycol ether derived phosphite [octyl polyethylene glycol phenylene-phosphite (OPGPP) IV] with precise cloud point was designed and synthesized by Jin et al. (30,31) (Scheme 1.3). The two-phase hydroformylation of styrene catalyzed by OPGPP/Rh(acac)$(CO)_2$ displayed excellent catalytic activity; high styrene conversion and high yield (99.6 and 99.3 %, respectively) were obtained at 80^{o}C, 5.0 MPa. The molar ratio of branched/normal aldehydes was 4.8 (30).

THERMOREGULATED PHASE TRANSFER CATALYSIS
General Principle

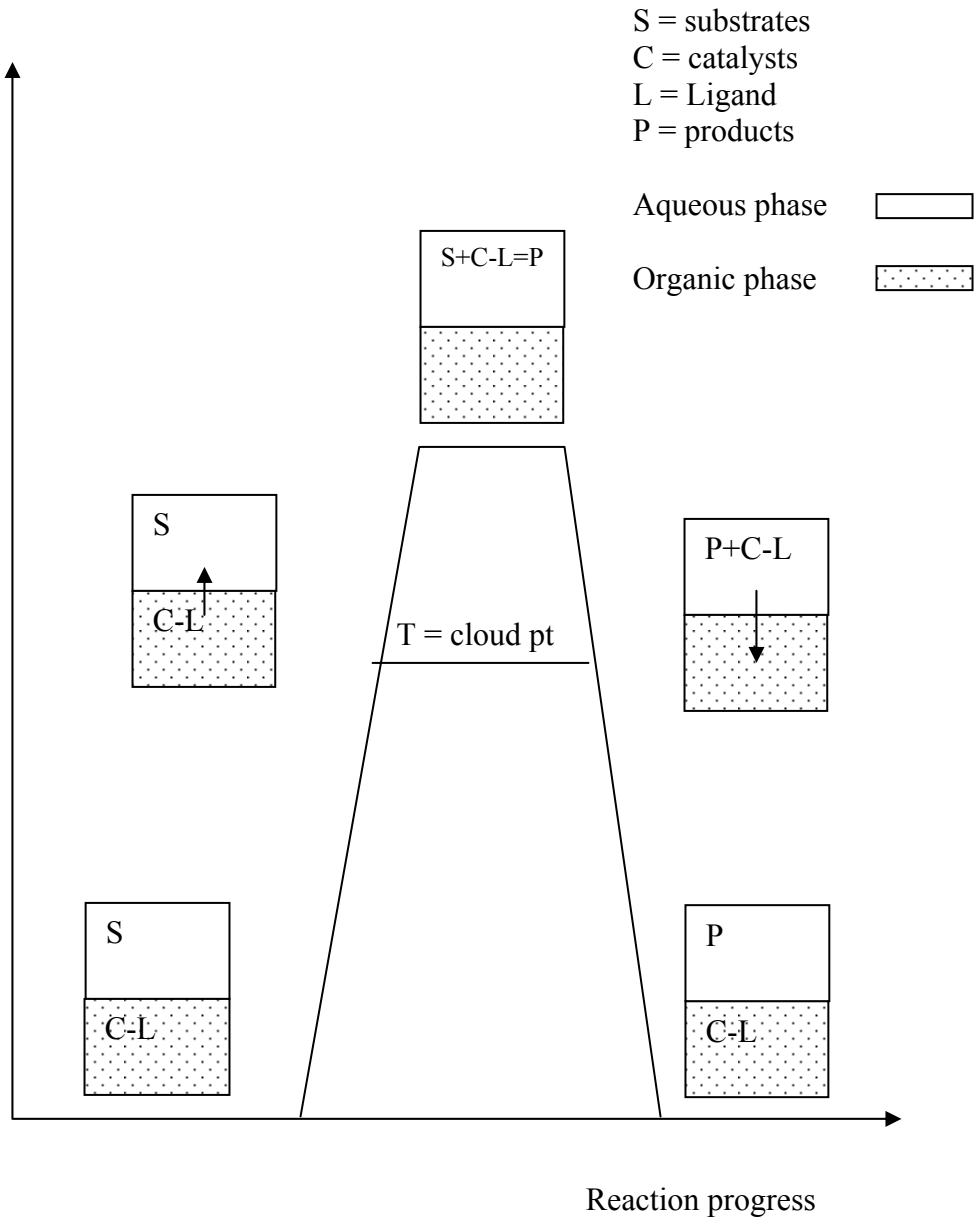
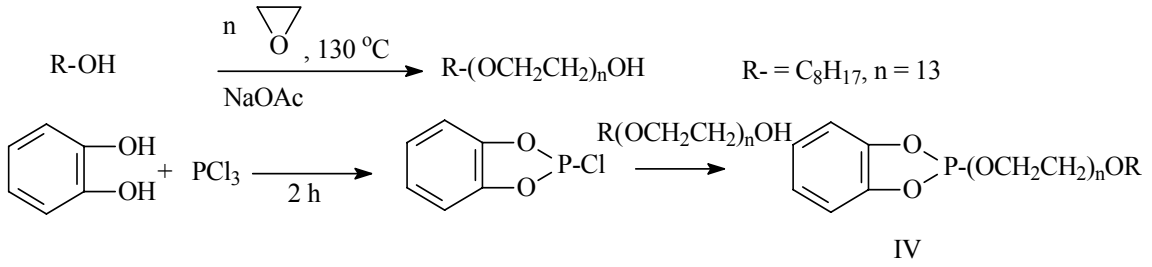
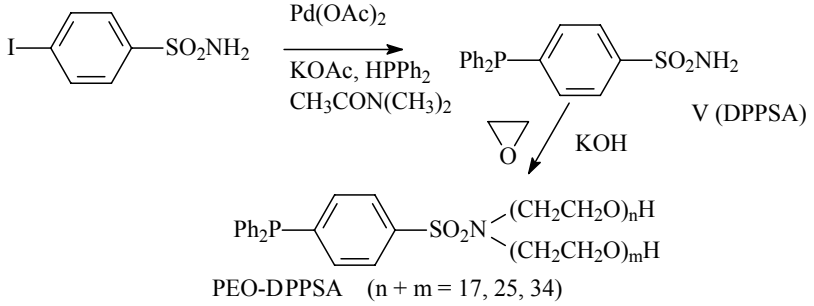


Figure 1.2



Scheme 1.3

Two novel water-soluble phosphines, N,N-dipolyoxyethylene-substituted-4-(diphenylphosphino) benzene sulfonamide and N,N-dipolyoxyethylene-substituted-2-(diphenylphosphino) phenyl amine (PEO-DPPSA and PEO-DPPPA, respectively) were also reported in 2001 and 2003 by Jin et al. (32,33), they used phosphorous-carbon (P-C) cross coupling reaction developed by Herd et al (34). Based on this synthetic strategy, DPPSA (V) and DPPPA were prepared by palladium catalyzed P-C coupling reaction between 4-I-$C_6H_4SO_2NH_2$ (and 2-I-$C_6H_4NH_2$ in the case of DPPPA) and Ph_2PH. The subsequent KOH-catalyzed ethoxylation of DPPSA with ethylene oxide leads to a novel PEO-DPPSA and PEO-DPPPA (Scheme 1.4). The rhodium complex of this phosphine ($RhCl_3.3H_2O$/PEO-DPPPA) exhibits high catalytic activity in the aqueous-organic hydroformylation of 1-decene. Recycling test shows that both the conversion of olefin and the yield of aldehydes are maintained higher than 94 % even after 20 cycles of the catalyst.



Scheme 1.4

The thermoregulated phase transfer catalysts such as OPGPP facilitate the aqueous two-phase hydroformylation of water-immiscible higher olefins and styrene, but there is a considerable loss of activity after four successive reaction runs owing to hydrolysis of the phosphite in water (30). To overcome this problem, one phase catalysis with facile separation termed as 'thermoregulated phase separable catalysis (TRPSC) was introduced by Z. Jin and his group in 2000 (35).

The general principle of TRPSC can be described as follow: At the beginning of the reaction and at room temperature, that is below the critical solution temperature (T < CST), the catalyst is insoluble in organic solvent and the organic phase is colorless. When heated to T > CST, the catalyst becomes soluble in the organic solvent and the whole system turned to be homogeneous with a brown color. At the reaction temperature (T > CTS), the reaction proceeds homogeneously. After the reaction, on cooling to room temperature (T < CST), the catalyst precipitates from the organic phase, which contains the products. Thus, by decantation, the products could be easily separated from the catalyst. So the process of TRPSC combines the advantages of homogenous and heterogeneous catalysis.

The concept of CST of nonionic tensioactive phosphine ligand PETPP [(P-OC_6H_4-$(OCH_2CH_2)_8$-OH]$_3$ with $RhCl_3.3H_2O$ as a catalyst has been primarily applied to the hydroformylation of higher olefins (1-dodecene) in organic monophasic catalytic system. The hydroformylation proceeds rather efficiently, with high conversion of olefins to yield over 92.5% of aldehydes under the optimum reaction conditions. The PETPP/Rh complex catalysts were recycled eight times and nearly no loss in activity was observed (36). Similarly, the hydroformylation of cyclohexene with PETPP/$RhCl_3.3H_2O$ catalytic

THERMOREGULATED PHASE-SEPARABLE CATALYSIS

BASIC PRINCIPLE

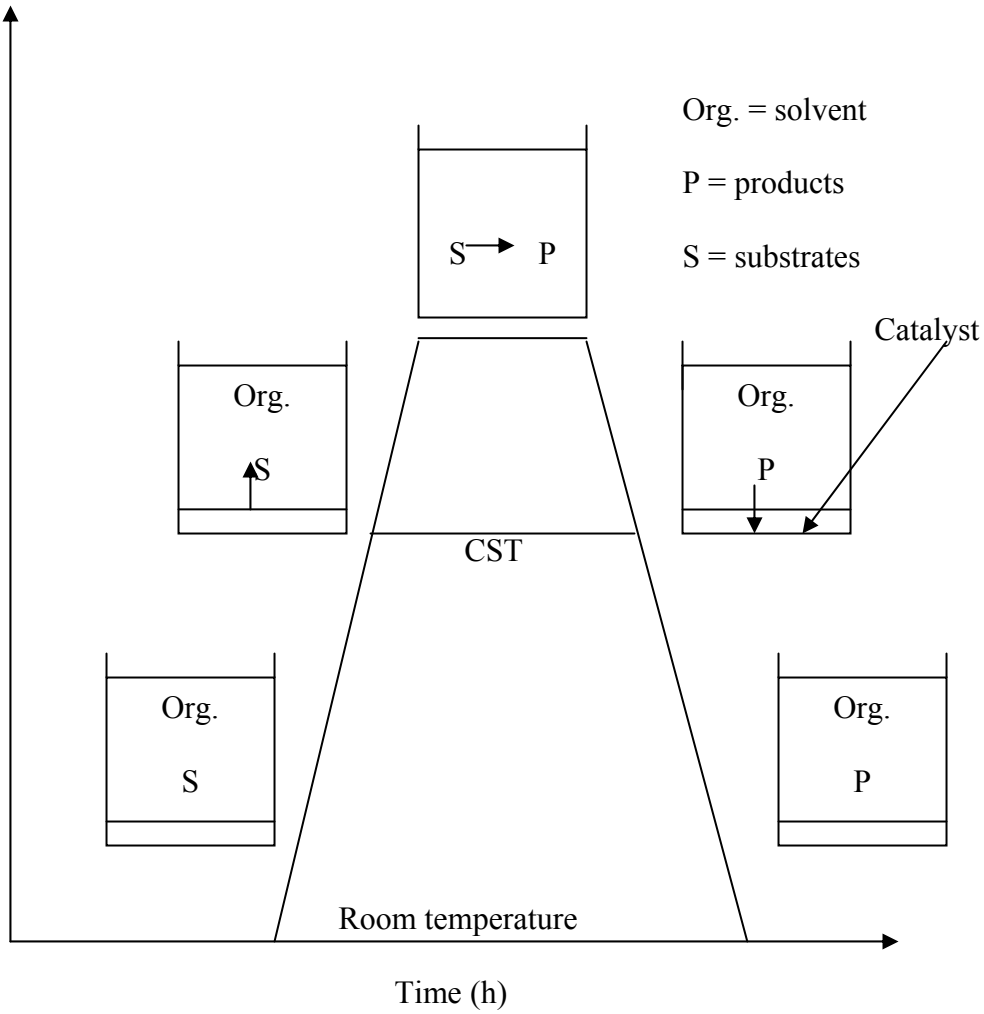


Figure 1.3

systems, at 130^{o}C, with toluene as a solvent was reported (37). A conversion and a yield of more than 98% were achieved after 7 h, and the catalysts were recycled at least five times without significant loss of activity.

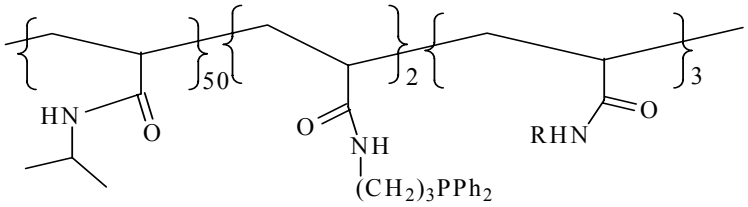
Jin et al. (38) have carried out studies on the effects of some different polyether phosphines on the hydroformylation and catalyst separation; the results show that *p*-Ph_2P-C_6H_4-$(OCH_2CH_2)_{16}OH$/Rh catalysts show considerable activity for the non-aqueous hydroformylation of 1-decene with heptane as solvent, while OPGPP (n = 58)/$Rh(acac)(CO)_2$ catalyzed the reaction with the highest conversion. Therefore, a conversion of 99.4% of 1-decene and a yield of 97.6% aldehydes were obtained after 4h (P = 5.0 MPa, T = 90^{o}C). In view of catalyst separation OPGPP, *p*-Ph_2P-C_6H_4-$(OCH_2CH_2)_{16}OH$, PEPTT (n = 8), and $Ph_2P(OCH_2CH_2)_{68}OPPh_2$ ligands and their rhodium complexes precipitated (as a viscous wax or mash) in a separate phase from heptane after reaction was cooled to room temperature. The catalyst is separated by simple decantation.

1.3.3 THERMOMORPHIC CATALYSIS

Liquid-liquid biphasic systems are frequently used in synthetic, catalytic and separation processes (39). The formation of a liquid-liquid biphasic system is due to the sufficiently different intermolecular forces of the two liquids resulting in limited or negligible solubility in each other. Thermomorphic catalysis or temperature-dependent multicomponent solvent systems is described using two solvents whose miscibility is temperature dependent. The separation in these systems relies on two ideas:

The first idea is that many binary systems and ternary solvent systems exhibit a reversible increase in miscibility with increasing temperature. For example, in some systems the originally biphasic mixtures become miscible and monophasic with mild

heating e.g. Figure 1.4. The second idea is that the catalytic system (catalyst and ligand) should have a strong preference for one phase under biphasic conditions. This will lead to a general route to separate a product from the homogeneous catalyst and to recover the catalyst by a simple liquid-liquid-phase separation followed by solvent removal to isolate the product (40). The idea of thermomorphic biphasic catalysis has its roots from the work of Bergbreiter et al. (41,42) with soluble poly(N-isopropylacrylamide) (PNIPAM) supports. Catalysts or substrates with PNIPAM (VI) can be readily recovered either by heating (water) or by solvent precipitation they are comparable in reactivity to their low molecular weight analogues when dissolved in water or organic solvent.



R = i-Pr; or H

PNIPAM (VI)

Pure ethanol and heptane are completely miscible at 25 ^{o}C. Addition of a polymer such as PNIPAM does not affect this miscibility. However addition of 10 % water (v/v) to the ethanol phase induces phase separation. The work with this system began with the realization that heating to 70 ^{o}C was sufficient to make this system miscible. Cooling reformed the initial biphasic system. Also the addition of a reagent that was exclusively soluble in one at room temperature will lead to a useful and potentially general scheme for catalyst/product/reagent separation. This realization was confirmed by simple experiments with the polymer supported dye VII. When this dye was added to a 2:1 (v:v) 90% aqueous ethanol/heptane mixture, the aqueous ethanol phase was bright red. The heptane phase

Diagrammatic representation of Thermomorphic catalysis

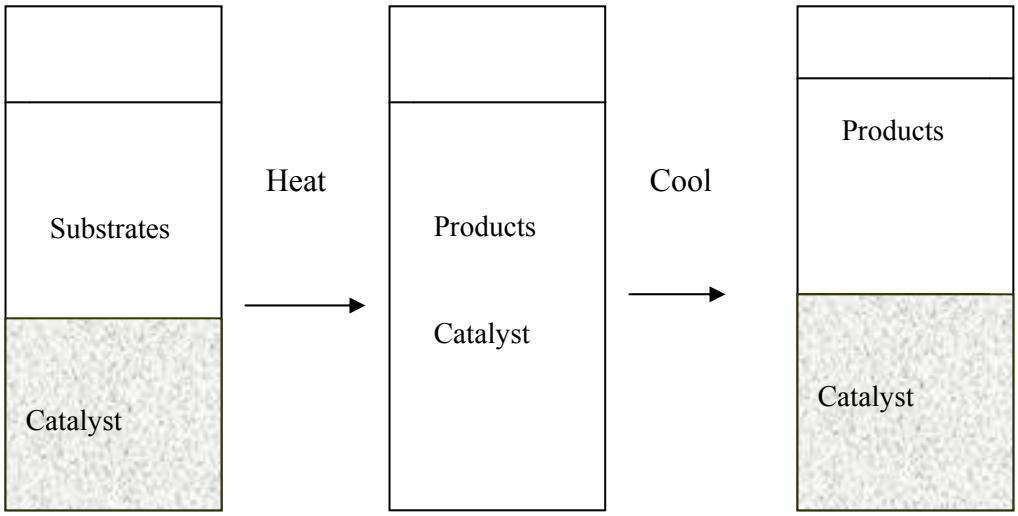
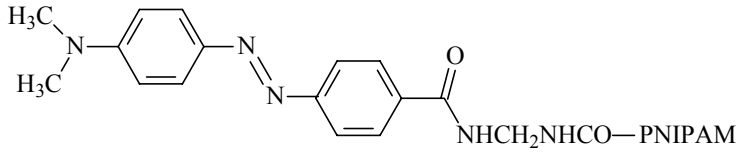


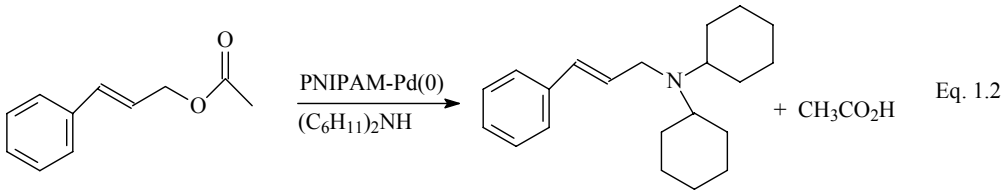
Figure 1.4

was colorless. On heating to 70 ^{o}C, the mixture became monophasic with the dye distributed throughout the solution. Cooling regenerated the original biphasic system with a1 being exclusively in the aqueous ethanol phase (43).



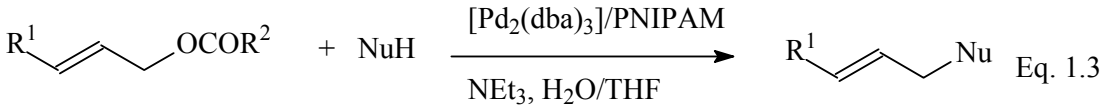
VII

To use this systems in catalysis, Bergbreiter et al. prepared PNIPAM-phosphine (VII) and complexed it with Rh (I). This catalytic system was used to study the hydrogenation of 1-octadecene and 1-dodecene. Thus, no detectable hydrogenation occurred at 22 ^{o}C (biphasic conditions). However, the hydrogenation did occur only when the biphasic mixture was heated to 70 ^{o}C (monophasic conditions). Similarly, PNIPAM-phosphine has been complexed to Pd(0), which is used in the coupling of dicyclohexylamine to cinnamyl acetate (Eq. 1.2). The catalyst remains active after four cycles.



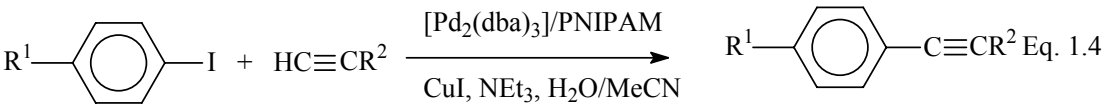
Eq. 1.2

The polymer-bound palladium (0)-phosphine catalyst based on water-soluble polymer PNIPAM in water, displays allylic substitution reactions (Eq. 1.3) and cross-coupling reactions of terminal alkynes with aryl iodides (Eq. 1.4) in good yield (86%-96%). The recycling of the catalyst proceeds by heating above the PNIPAM's cloud point or by precipitating by adding hexane to the reaction mixture (40).



Eq. 1.3

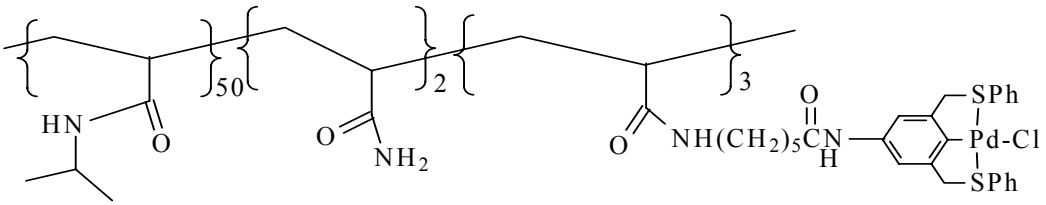
R^1 = H, Ph
R^2 = CH_3, OCH_2CH_2COONa
NuH = Et_2NH, piperidone



Eq. 1.4

R^1 = H, OMe, COONa
R^2 = Ph, $CH_2(CH_2)_2CH_3$, $C(CH_3)_2(OH)$

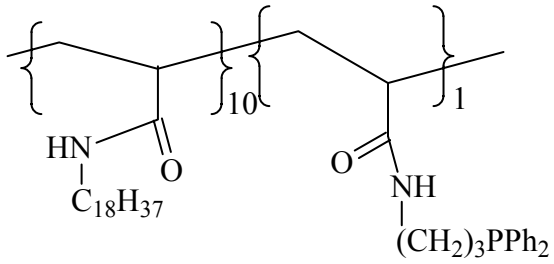
Phosphine-ligated Pd(0) catalyst is air sensitive, therefore steadily deactivation occurs via adventitious oxidation during the recycling. This practical limitation for the catalyst recycling could be avoided by using a more stable tridentate sulfur-carbon-sulfur (SCS) Pd(II) catalyst (PNIPAM-SCS-PdCl VIII). Such palladacycles are thermally and oxidatively robust. At 120 ^oC in DMF solution, they catalyze the Heck reaction of a number of aryl iodides and acceptor alkenes in air. These catalysts can also readily be bonded to poly-(ethylene glycol). Such PEG-bond SCS catalysts could be recovered by solvent precipitation (44).



PNIPAM-SCS-Pd-Cl (VIII)

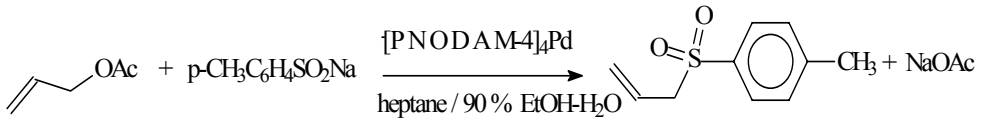
However, the chemistry of what was discussed above is limited to non-polar products or by-products, but for polar products, non-polar polymer support such poly(N-

octadecyl-acrylamide) (PNODAM-4, IX) was designed to quantitatively stay in the non-polar phase of the biphasic phase of the mixture (an inverse thermomorphic separation).



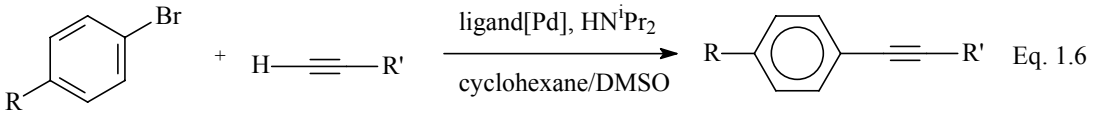
PNODAM-4 (IX)

Pd(0) bond to PNODAM-4 was used for allylic sulfone synthesis under biphasic conditions and the catalyst could be recycled five times (45).



Eq. 1.5

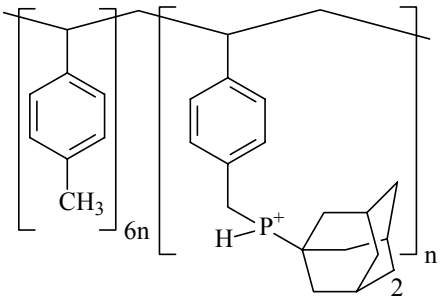
Plenio and Datta demonstrated that Pd(0) complexes with $BnP(1\text{-}Ad)_2$ (Ad = adamantly, X), which is sterically demanding and electron-rich phosphine are highly active catalyst suitable for room temperature Sonogashira coupling reaction of aryl bromides with alkynes (46) (Eq. 1.6).



Eq. 1.6

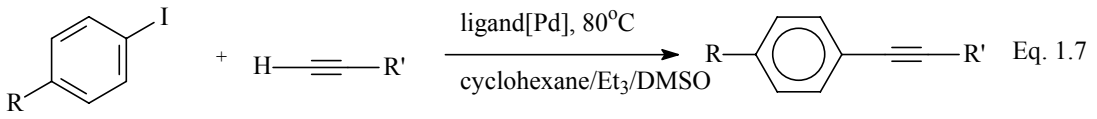
R = CH_3CO, OME, or CO_2Et, R' = Ph or hexyl

ligand =



X

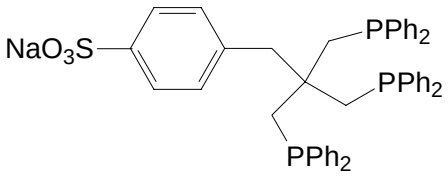
Kollhofer and Plenio have initiated and developed polymer-tagged palladium-phosphine complexes [MeOPEG-O-$CH_2C_6H_4$-CH_2-PPh_2] and MeOPEG-O-$CH_2C_6H_4$-CH_2-$P(ad)_2$ for carbon-carbon forming reaction such as Heck, Suzuki and Sonagashira coupling (47) (Eq. 1.7).



Eq. 1.7

R = 4-MeO, 4-Me, or 4-Cl R' = Ph or Et_3Si, Ligand = $MeOPEGOC_6H_4PPh_2$

The sulphonated TRIPHOS (sulphos XI) forms the complex $[Rh(COD)(sulphos)]^+$ with rhodium precursor. 1 mol.% of the complex catalyses the hydroformylation of 1-hexene in aqueous methanol/isooctane at 80 °C, CO/H_2 pressure of 30 bar to give heptanal and 2-methylhexanal in the ratio 69:31 (48).



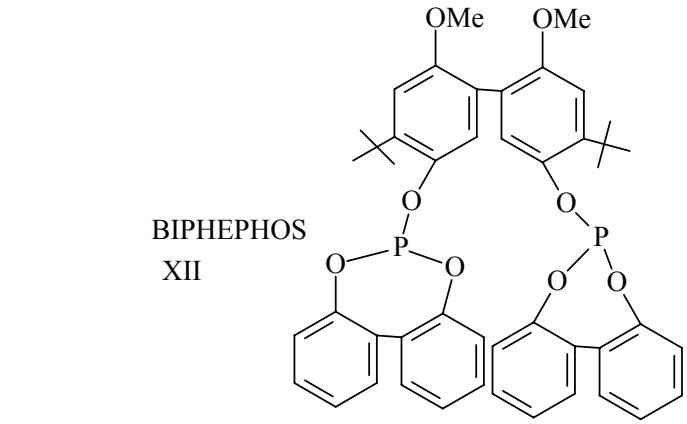
sulphos (XI)

All the catalytic system discussed so far involved the use of special tagged ligands and the syntheses of these ligands are often difficult and complicated. The idea of carrying out a catalytic reaction with a recycling based on temperature-dependent multicomponent solvent system (TMS), without the use of any specially tagged ligand was introduced by Behr and Toslu (48,49). They hydrosilylated 10-undecenate with triethoxylsilane, using PC / cyclohexane / toluene solvent system and hexachloroplatinic acid catalyst.

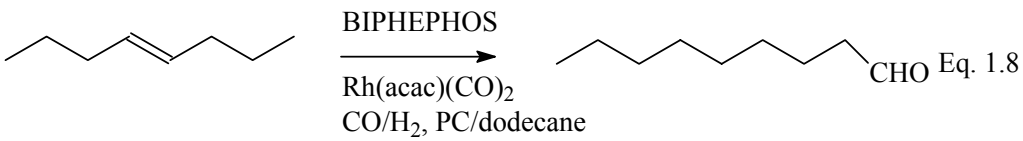
Similarly, Behr and Fangewisch carried out rhodium-catalyzed cooligomarization of sunflower fatty acid methyl ester (SFAME) and ethylene, using organic halide as

promoting agent in PC/SFAME/dioxane solvents system. The catalytic system was recycled four times without loss in the catalytic activity (25).

Recently, the isomerization and the hydroformylation of *trans*-4-octene to n-nonanal was achieved using [Rh(acac)$(CO)_2$] and BIPHEPHOS (XII), in both monophasic PC and PC/docecane/xylene multicomponent solvents system. The reaction was carried out at 125 ^oC, under 10 bars of CO/H_2 (1:1) pressure (50).



BIPHEPHOS
XII



Eq. 1.8

1.3.4 HETEROGENIZED HOMOGENEOUS CATALYSIS

Homogeneous catalysis is of interest due to its high activity and selectivity at milder reaction conditions for a wide variety of reactions (51). However, their practical applications have been limited by difficulties in achieving industrially viable catalyst-products separation (52). The immobilization or heterogenization of the homogeneous catalysts on inorganic support materials can be achieved by various methods. These

methods can be classified by the interaction between catalytically active component and support (53).

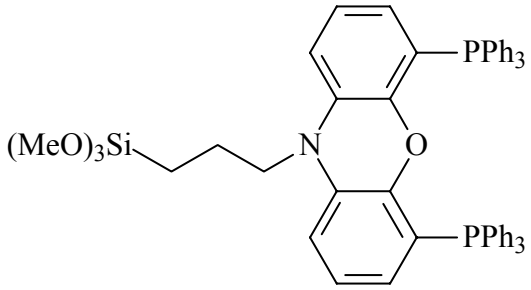
A. The active component is chemisorbed on the support. This category includes many well know catalysts, which can be synthesized by the impregnation of the metal salts on inorganic supports e.g. alumina, silica or zeolites (54).
B. The active component is encapsulated or encaged within the structure of the support. This is generally used for the immobilization of metal complexes (55).
C. The active component is physiosorbed on the support. The catalyst, consisting of a metal center and organic ligands, the catalyst is immobilized through the interaction between functional groups of the ligands and the surface of the supported material (56). “Supported liquid-aqueous phase catalysts” belong to this group.

Zeolites and Zeotypes (molecular sieve) owing to their varying intrinsic properties such as acidity, channel sizes, high surface area, thermal stability, chemical stabilities and channel structure (shape selectivity) have been used in oil refining, petrochemical and fine chemical industries. But the limitation of pore sizes (less than 13Å) of these microporous materials demanded a search for new materials with lager pore sizes such as MCM-41 and related materials (51).

Immobilization of a dinuclear rhodium(II) acetato complex with bridging *ortho*-metalated phosphine ligands on amorphous silica supports as well as a mesoporous MCM-41 support resulted in useful catalysts for hydroformylation of styrene and 1-

decene. The effect of recycling on the conversion of the olefins and on the branched–normal selectivity of the hydroformylation products was studied (57).

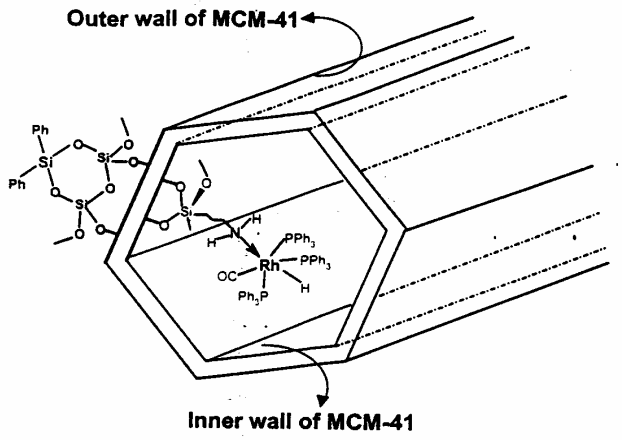
A polysilicate immobilized rhodium complex with ligand (XIII) was found to perform as a selective hydroformylation catalyst showing an overall selectivity for the linear aldehyde of 94.6% in the case of the hydroformylation of 1-octene at 80°C and 50 bar CO/H_2 1:1. In addition, the formation of 1-nonanol (3.6% at 20% conversion) was observed via the hydrogenation of the corresponding aldehyde. The addition of 1-propanol completely suppresses the reduction reaction. The reduction reaction becomes prevalent if the atmosphere is changed from CO/H_2 to H_2. Thus, by simple changes in the reaction conditions, a reversible switching of the catalyst mode between a hydroformylation, a hydrogenation and a hydroformylation/hydrogenation cascade catalyst was demonstrated (58).



Silica diphosphine ligand (XIII)

Functionalization of MCM-41 with 3-aminopropyltrimethoxyesiline (APTS), and subsequent encapsulation and anchoring of $HRh(CO)(PPh_3)_3$ in the mesoporous material was recently reported (51). This unique approach of passivation of the external surface silanol (Si-OH), by reacting with controlled amount of Ph_2SiCl_2 and subsequent treatment with APTS, resulted to selective functionalization of the inner-surface. Thus, the initial

treatment of mesoporous with Ph_2SiCl_2 compelled anchoring of APTS, as well as Rh complex selectively inside the mesopore channels.



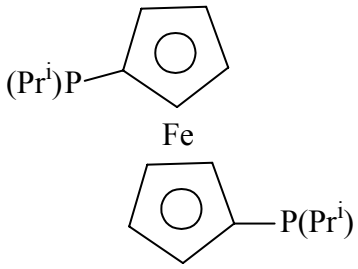
Functionalization of MCM-41 (XIV)

To date, virtually every example of such supported homogeneous catalysts has involved some method for placing a ligand on a solid material and then using this 'heterogenized' ligand to prepare a catalytic complex. Within this form of attachment, the metal atom could be removed by a ligand exchange reaction possibly with some of the products, substrate molecules or other species present in the reaction mixture. In most cases, the activity and the selectivity of these heterogenized complexes were lower than those observed with the corresponding homogeneous species and also there is gradual loss of activity and selectivity with number of cycles. This approach, which requires the incorporation of the ligand onto a solid material, is particularly difficult to apply with most of the chiral ligands used in the highly efficient enantioselective homogeneous catalysts in use today (59).

To solve this problem, Augustine et. al. (60) developed an innovative strategy for anchoring homogeneous catalysts to a support through phosphotungstic acid. In this method Rh(Di-Pamp) was anchored to phosphotungstic acid functionalized alumina. The

catalyst was reused fifteen times in asymmetric hydrogenation of methyl 2-acetamidoacrylate, with a very little leaching of the catalyst.

Similarly, Rh(I) catalyst bearing the diphosphine 1,1`-bis(diisopropylphosphino)-ferrocene (DiPFc) (XV) was immobilized on phosphotungstic acid treated alumina or silica. The catalyst was used for efficient and selective hydrogenation of a range of functionalized aldehydes, as well as alkenes and alkynes, under mild conditions. The catalyst was also recycled several times (61).



DiPFc

1,1'-bis(diisopropylphosphino)-ferrocene (DiPFc) (XV)

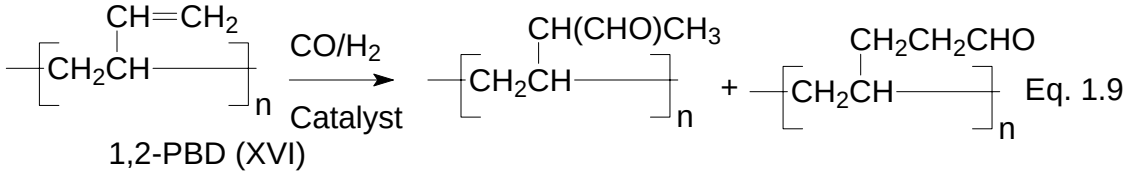
$Rh_4(CO)_{12}$ have been successfully anchored to MCM-41(PPh_2), MCM-41(NH_2) and MCM-41(SH). The effect of the three donor ligands on the catalytic hydroformylation of cyclohexene were compared (62). In recent years, the immobilization of Rh-PPh_3 complexes onto amino-functionalized MCM-41 and MCM-48 as efficient heterogeneous catalyst for higher olefin hydroformylation has been reported by several groups (63,64).

Recently, a novel approach to immobilizing homogeneous catalysts on solid supports has been reported, in which the Wilkinson's hydroformylation catalyst complex was tethered through heteropolyacid to zeolites (65). The process resulted in an excellent stability, reusability and even improved activity of the rhodium catalyst. The new

heterogenized homogeneous catalysts are being at least as active as the homogeneous species and capable of being re-used many times with little loss in activity and selectivity.

1.4 HYDROFORMYLATION OF POLYBUTADIENE

The chemical modifications of polymers include reactions such as cross linking, grafting, degradation, oxidation, isomerization, and cyclization. Their principal utility is to produce desirable physical and chemical properties within polymers that are often difficult or impossible to achieve with standard polymerization techniques. Polymers generally used as substrates for chemical modifications are unsaturated polymers or polymers containing olefinic unsaturation within the polymer structure. One of the most interesting methods for chemically modifying polymers is the addition of functional groups onto backbone polymers. McManus and Rempel (66) reviewed some chemical modification processes such as hydrogenation, hydrosilylation, hydrocyanation, hydrocarboxylation, hydroformylation and hydroxymethylation for diene-based polymers and copolymers. The catalytic hydroformylation of unsaturated polymers is a process by which aldehyde groups are introduced into the backbone polymer by a treatment with H_2 and CO in the presence of a catalyst (Eq. 1.9).

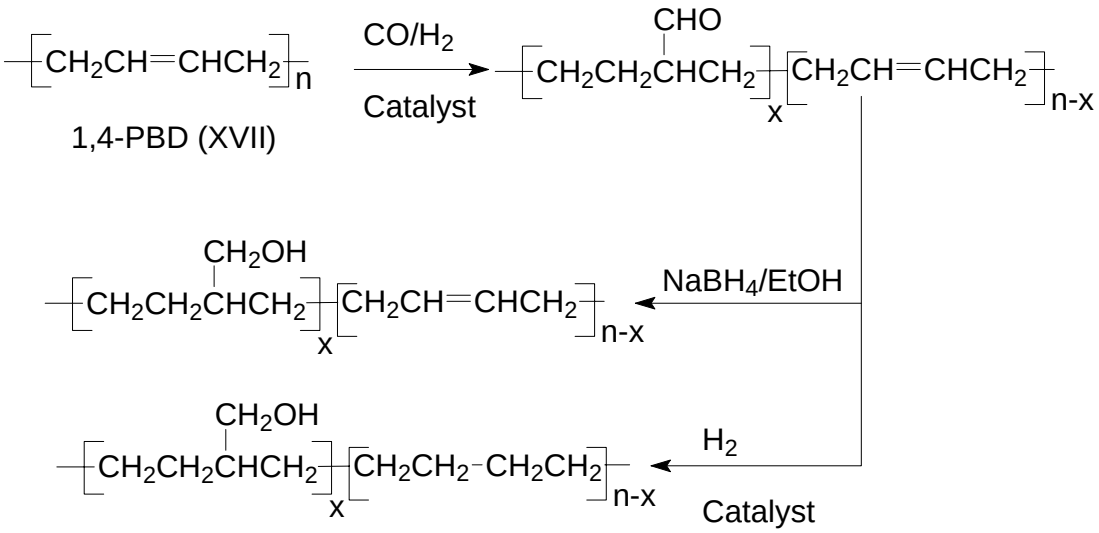


Eq. 1.9

The common catalyst generally used for this process is a Co or Rh complex (67-75). The most effective catalysts for the hydroformylation of a double bond are rhodium complexes. Hydridocarbonyltris(triphenyl phosphine)- rhodium [$HRh(CO)(PPh_3)_3$] is a catalyst that has been widely used for the hydroformylation of olefins and polymers under moderate conditions (68-76). There are many applications for hydroformylated polymers, such as protective coatings (77-80), smooth and wrinkle-free films (81), and sizing for glass fibers (82). Because of the reactivity of the aldehyde group, the hydroformylated products can be reacted via further reactions to produce nitrile, alcohol, acetate, and amine functionalities. The most often used subsequent reaction is hydrogenation, which produces a polymer with hydroxyl methyl groups. The hydroxymethylated product can be used as a substrate for producing polyurethane [82]. Most studies of the hydroformylation of diene polymers, that is, polybutadiene (PBD) and poly(styrene butadiene) (SBR), were carried out in the presence of rhodium catalysts. However, the earliest study showed that the hydroformylation of 1,4-PBD (XVII) and high-styrene SBR could be achieved at high pressures and temperatures with a cobalt catalyst (67) but there was considerable gel formation during this process.

The first report of the use of $HRh(CO)(PPh_3)_3$ in the hydroformylation of a polypentenamer was by Sanui et al. (68) and the reaction was carried out under moderate conditions with no gel formation. Later, Tremont and Remsen (69) studied the hydroformylation of low-molecular-weight 1,2-PBD (XVI) and 1,4-PBD in the presence of $HRh(CO)(PPh_3)_3$ with excess triphenyl phosphine. Scott and Rempel (70) investigated the kinetics of the hydroformylation of SBR with the same catalyst. Furthermore, they postulated a possible reaction mechanism and presented an understanding of the catalyst

species in solution. Azuma et al. (71) reported the preparation of a functional polydiene by a two-step process for the hydroxymethylation of a polypentenamer and cis-1,4-PBD. The initial reaction was hydroformylation with $HRh(CO)(PPh_3)_3$, followed by the reduction with sodium borohydride such as a reducing agent or by catalytic hydrogenation with hydrogen (Scheme 1.5).



Scheme 1.5

The higher conversion led to a problem of solubility due to the cross linking of the hydroxyl group with the formyl group. The use of a selective reducing agent for the reduction of the formyl groups without hydrogenation at double bonds was critical. In the same manner, McGrath et al. (72) reported the synthesis of a novel ethylene–propylene–diene monomer and PBD polyols. The hydroformylation reaction was accomplished at high pressures and temperatures, and later the aldehyde groups were reduced to hydroxymethyl groups on the polymer. They also reported the production of polyurethane by a further reaction with diisocyanates. The synthesis and characterization of

hydroformylated 1,2-PBD were also reported by Mohammadi (73), and the subsequent hydrogenation was achieved with $RuCl(C_6H_5COO)$-$(CO)(PPh_3)_2$ as the catalyst. Sibtain and Rempel (74) investigated this hydroformylation and hydroxymethylation of SBR with $HRh(CO)(PPh_3)_3$ and $HRuCl(CO)(PPh_3)_3$, respectively. Moreover, they reported the development of IR calibration curves to estimate the degree of hydroformylation.

All previous investigations reported the use of low-molecular-weight polymers with a weight-average molecular weight (Mw) of less than 200,000 for hydroformylation with moderate conversions. Recently, Chen et al. (75) studied the hydroformylation of higher molecular weight styrene–butadiene copolymers (Mw~200,000) under more severe reaction conditions in the presence of various rhodium catalysts, and conversions greater than 50 % were achieved. The main purpose of this study was to prepare and characterize the hydroformylation products of high-molecular weight cis-1,4-PBD. Because of its structure, cis-1,4-PBD can serve as a primary material for the further investigation of other polydienes such as synthetic cis-1,4-polyisoprene and natural rubber. This work was aimed of studying the detailed kinetics of the hydroformylation of cis-1,4-PBD to obtain further understanding of the reaction at high conversions and conditions, and this led to the postulation of a reaction mechanism.

1.5 Conclusion

The above examples have shown that there is a considerable activity in searching for ways to achieve selectively separation and recycling of homogenous catalyst in the rhodium catalyzed hydroformylation of alkenes.

1.6 Objectives

The present proposal deals with hydroformylation of unsaturated substrates, as well as the recycling of the catalysts and the main objectives are:

1- To develop liquid-liquid biphasic system suitable for hydroformylation reactions and recycling (i.e. thermomorphic biphasic hydroformylation).

2- To synthesize suitable-water soluble polyethylene oxide ligand, that will be used in aqueous/organic thermoregulated phase transfer catalysis and thermoregulated phase separable catalysis.

3- To investigate the best catalytic system suitable for hydroformylation of polybutadiene.

4- To synthesize and investigate the catalytic behavior of rhodium catalysts immobilized in MCM-41.

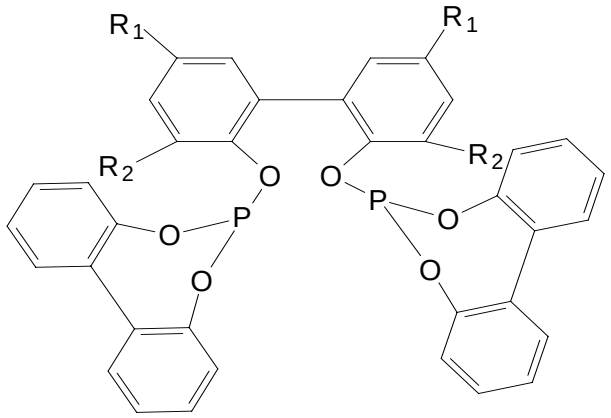
CHAPTER 2

2.0 SOLUBLE RHODIUM CATALYZED HOMOGENEOUS HYDROFORMYLATION OF ALKENES

2.1 Introduction

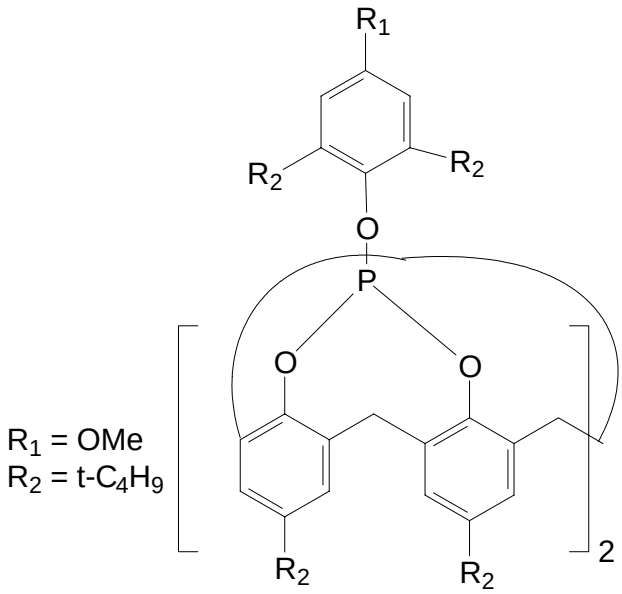
The rhodium-catalyzed low-pressure hydroformylation of olefins is, in terms of production volume, one of the most important homogeneous catalysis processes (83). Since Wilkinson's discovery that through addition of phosphine ligands to rhodium-catalysts, the hydroformylation can be now performed at lower temperature and pressure (11). Phosphite ligands and especially bulky phosphites are very useful in rhodium catalyzed hydroformylation because of the higher reaction rates obtained compare to triphenylphosphine (84). An important drawback however is the loss of selectivity. One way to improve the selectivity was by changing to diphosphite system. It was only after the first reports from Bryant and coworkers that phosphites were recognized as a new generation of promising ligands in rhodium catalyzed hydroformylation of alkenes (85). High regioselectivities with diphosphite ligands (XVIII) (with 2,2'-biphenol backbone) in the rhodium catalyzed hydroformylation of functionalized alkenes has been published (86,87).

The hydroformylation of 1-octene catalyzed by $Rh(CO)_2(acac)$ with chelated bisphosphites (calix[4]arene backbone) (XIX) gave 99.5 % nonanal at 80-100 ^{o}C and 5-20 bars (83). The naturally occurring cinchona alkanoid, chiconidine, quinine and quinidine were hydroformylated to terminal aldehyde derivatives in 87 %, 81 % and 85 %



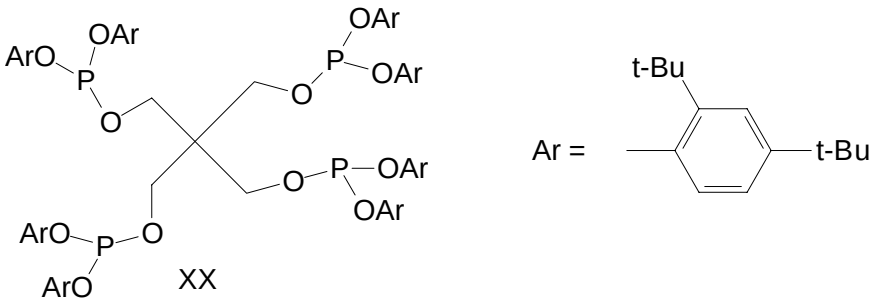
XVIII

respectively, using $Rh(CO)_2(acac)$ / tetraphosphite (XX) catalyst at 90 ^oC and 20 bars CO / H_2 in toluene (88).

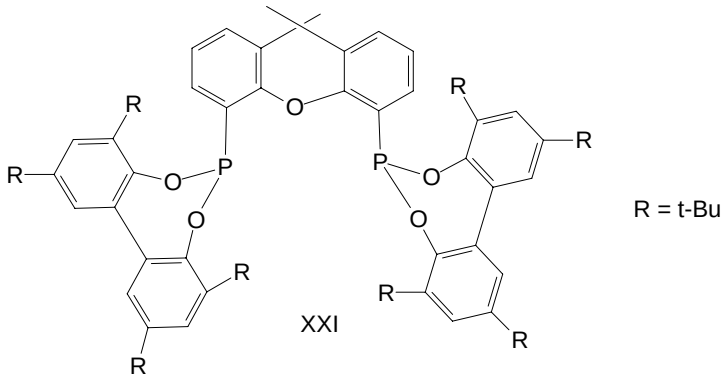


XIX

The isomerizing hydroformylation of *trans*-4-octene in toluene using $Rh(CO)_2(acac)$/BIPHEPHOS (XII) catalyst was carried out with the conversion of 75 % and a selectivity to the linear aldehydes of 94 % (25).

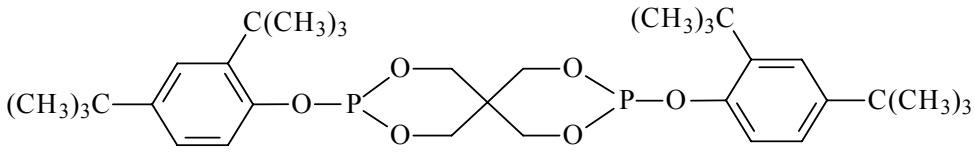


Sterically constrained diphophonite ligands with xanthene backbone (XXI) were used for the rhodium-catalyzed hydroformylation of 1-octene and 2-butene. High activities were obtained for 1-octene, with good selectivity to the linear aldehyde and for the 2-butene the selectivity for the n-pentanal was 62 % (89).



Hydroformylation for a series of alkenes and alkynes have been carried out using heteronuclear rhodium-tungsten catalyst, $(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$. The results of these reactions have been compared with the corresponding reaction using $[Rh(OAc)_2]_2$ as catalyst precursor. Four rhodium-based catalyst systems $(OC)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, $(OC)_2RhMo(CO)_3(C_5H_4PPh_2)_2$, $(OC)_2RhW(CO)_3(C_5H_4PPh_2)_3$, and $[Rh(OAc)_2]_2/PPh_3$ have been used in the hydroformylation of 1-hexene, styrene and some phosphino-, amino- and amido-alkenes. In general the catalysts showed very similar activity and selectivity (90).

The use of heteropolyacids in conjunction with rhodium catalyst has not been fully investigated in the hydroformylation reactions. Similarly, bis(2,4-di-tert-butyl)pentaerythritol diphosphite (alkanox P-24) (XXII) which has been used as antioxidant in the stabilization of polymers (91), has not been used as a ligand in hydroformylation reaction.



bis(2,4-di-terbutylphenyl)pentaerythritol diphosphite (XXII)

In this chapter, the results of three catalytic systems used in the homogenous catalytic hydroformylation of alkenes are presented:

1) Catalytic system A: $Rh_6(CO)_{16}$/HPA-W_{12}/CO/H_2/40^oC/16h
2) Catalytic system B: $Rh_6(CO)_{16}$/$P(OPh)_3$/CO/H_2/60^oC/6h
3) Catalytic system C: $Rh(CO)_2(acac)$/Ligand XXII/CO/H_2/120^oC/1h

2.2 Experimental Section

2.2.1 General

$HRhCO(PPh_3)_3$ and other rhodium complexes were purchased from Strem Company. Alkenes were purified by passing through neutral alumina, propylene carbonate was purchased from BDH chemicals and used without purification, and all other solvents were purchased from Sigma–Aldrich and were purified prior to usage.

^1H and ^{13}C NMR spectra were recorded on 500 MHz Joel 150 NMR machine. Chemical shifts were reported in ppm relative to tetramethyl silane (TMS) using $CDCl_3$. Gas chromatography analyses were realized on HP-6890-plus GC equipped with 30 m capillary column (HP-1).

2.2.2 General procedure for homogeneous hydroformylation of alkenes

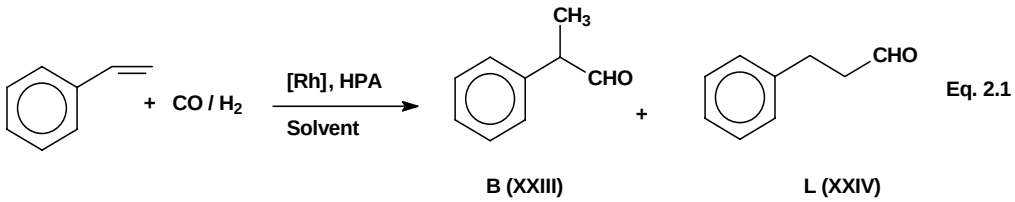
A typical experimental procedure is as follow: 5.0 mmol of substrate, 0.005 mmol of [Rh] and 0.060 mmol of monodentate ligand or its equivalent of bidentate or 0.01mmol of HPA-W_{12} were dissolved in 5.0 ml of the solvent and placed in the glass liner of a 25 ml Parr autoclave. The autoclave was purged three times with carbon monoxide, pressurized with the required psi CO + H_2 and then heated in an oil bath with temperature controller fixed at required temperature. After the reaction time, the mixture was cooled to room temperature and the aldehydes are identified by GC and GC-MS using n-decane or anisole as an internal standard. The ^{1}H and ^{13}C NMR of the products gave excellent spectral data compared to authentic samples.

2.3 Results and discussions

2.3.1 Homogeneous hydroformylation of aryl alkenes by rhodium catalysts

The homogeneous hydroformylation reaction of styrene derivatives produces important products that may have interesting applications in industry, such as anti-inflammatory products from branched aldehydes and alcohols from linear isomers. The reaction optimization was carried out using styrene as a model substrate of aromatic alkenes. The rhodium complex $Rh_6(CO)_{16}$ showed the highest catalytic activity in the presence of the heteropolyacid $H_3PW_{12}O_{40}$ (HPA-W_{12}) in THF as a solvent at 40 ^{o}C and in the absence of any phosphine ligand. The ratio of syngas CO / H_2 was fixed as 1/1 with 600 psi of a total pressure of the syngas at room temperature. The effects of the amount of HPA-W_{12}, the temperature, the type of solvent, the CO / H_2 ratio, and the type of rhodium catalyst and the type of the heteropolyacids have been carefully studied in order to determine the most suitable conditions of hydroformylation prior to study the

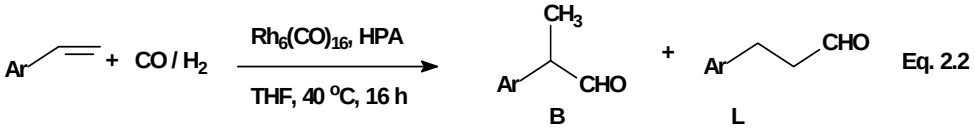
hydroformylation of other aryl alkenes. The hydroformylation of styrene usually leads to the branched aldehyde, 1-phenyl-1-propanal (**B**) (XXIII), and the linear aldehyde, 2-phenyl-1-propanal (**L**) (XXIV) (Eq. 2.1). However, other by-products such alcohol or hydrogenated products may also be formed.



2.3.2 Hydroformylation of Styrene catalyzed by $R_6(CO)_{16}$/HPA-W_{12}. Effect of the type and amount of heteropolyacid

The effect of the amount of the heteropolyacid $H_3PW_{12}O_{40}$, xH_2O **(HPA-W_{12})** as a co-catalyst in the hydroformylation of styrene was studied in the presence of the rhodium catalyst **($Rh_6(CO)_{16}$)** at 600 psi of syngas (CO / H_2=1/1) and 40 ^oC in THF as a solvent. The results of the study on the effect of the amount of the heteropolyacid HPA-W_{12} are summarized in the Table 2.1. The conversion of styrene was 61 % in the absence of HPA-W_{12} (Table 2.1 entry 1) and the selectivity toward the branched aldehyde **B** was high (92 %). The conversion of styrene into aldehydes increased from 61 % to 74 % with the addition of 0.0025 mmol of the co-catalyst **HPA-W_{12}** (Table 2.1, entry 2)**.** The increase in the amount of the co-catalyst to 0.010 mmol improved the conversion to 97 % (Table 2.1, entry 4). The selectivity toward the branched aldehyde was maintained extremely high (92-94 %). Surprisingly, the further addition of the heteropolyacid HPA-W_{12} inhibited the reaction of hydroformylation of styrene; the conversion of styrene dropped to 75 % by using 0.030 mmol of HPA-W_{12} (Table 2.1, entry 6). The role of the heteropolyacid **HPA-**

Table 2.1 Hydroformylation of Styrene catalyzed by $R_6(CO)_{16}$/HPA-W_{12}: Effect of amount and the type of the heteropolyacid.[a]



Entry	Co catalyst mmol	Conversion[b] %	Product Distribution[c] % B / L
1	**$H_3PW_{12}O_{40}$(0.00)**	61	92 / 8
2	**$H_3PW_{12}O_{40}$(0.0025)**	74	93 / 7
3	**$H_3PW_{12}O_{40}$(0.0050)**	90	93 / 7
4	**$H_3PW_{12}O_{40}$(0.010)**	97	94 / 6
5	**$H_3PW_{12}O_{40}$(0.020)**	88	92 / 8
6	**$H_3PW_{12}O_{40}$(0.030)**	75	93 / 7
7	**$H_3PMo_{12}O_{40}$(0.010)**	90	93 / 7
8	**$H_4SiMo_{12}O_{40}$(0.010)**	90	91 / 9
9	**$(NH_4)_3PMo_{12}O_{40}$(0.010)**	70	90 / 10
10	**$(NH_4)_3PW_{12}O_{40}$(0.010)**	76	92 / 8
11	**$H_5PMo_{10}V_2O_{40}$(0.010)**	74	94 / 6
12	**$H_7PMo_8V_4O_{40}$(0.010)**	78	91 / 9

a) Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.010 mmol), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO/H_2 = 1/1), 40 °C, 16 h.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^{1}H NMR.

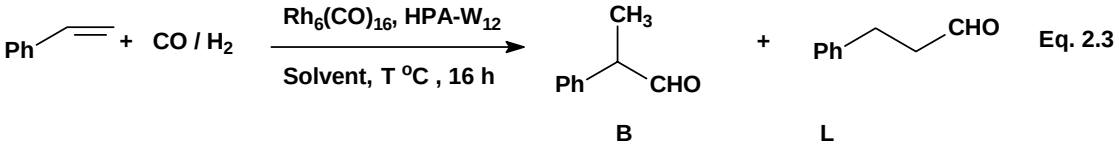
W_{12} in the hydroformylation of styrene-catalyzed by rhodium (I) was most probably in the formation of an active intermediate [W-Rh] that has higher solubility and catalytic activity at low temperature.

Other heteropolyacids of Keggin structure such as $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ used instead of **HPA-W_{12}** gave also high conversions of styrene (90 %) (Table 2.1, entries 7,8). However, the ammonium salts $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$ (Table 2.1, entries 9,10), and the heteropolyacids that have vanadium in their structures of (**HPA-n)**, such as **$H_5PMo_{10}V_2O_{40}$** and **$H_7PMo_8V_4O_{40}$** (Table 2.1, entries 11,12), the conversions of styrene decreased to 74 to 78 %. The selectivity toward the branched aldehyde **B** was high (> 90 %). It seems clearly that these later mixed polyoxometallates had no effect on the occurrence of the reactions and most probably do not form complexes with $Rh_6(CO)_{16}$ under the experimental conditions.

2.3.3 Hydroformylation of styrene- catalyzed by $R_6(CO)_{16}$/HPA-W_{12}. Effect of the Temperature and the of type of Solvent

The catalyst systems combining $Rh_6(CO)_{16}$ and HPA-W_{12} were carefully studied at different temperatures (Table 2.2). We were surprised to observe that the hydroformylation reaction of styrene occurred with the system $Rh_6(CO)_{16}$ / HPA-W_{12} even at room temperature (approximately 25 ^oC) with 42 % of conversion of styrene and 98 % selectivity in branched aldehyde after 16 h of reaction (Table 2.2, entry 1). The reaction was complete at 45 ^oC and the selectivity in **B** still high (92 %) (Table 2.2, entry 2). However, the selectivity of reaction dropped at temperature higher than 60 ^oC to reach 75 % at 80 ^oC (Table 2.2, entries 5,6). It is clear that the highest catalytic activity was

Table 2.2 Hydroformylation of Styrene catalyzed by $Rh_6(CO)_{16}$ / HPA-W_{12}: Effect of temperature and type of solvent.[a]



Entry	T °C	Solvent	Conversion[b] %	Product Distribution[c] B / L %
1	**25**	THF	42	98 / 2
2	**40**	THF	97	94 / 6
3	**45**	THF	100	92 / 8
4	**50**	THF	100	90 /10
5	**60**	THF	100	86 / 14
6	**80**	THF	100	75 / 25
7	**100**	THF	100	57 / 43
8	40	**DME**	92	97 / 3
9	40	**1,4-dioxane**	88	95 / 5
10	40	**CH_2Cl_2**	84	92 / 8
11	40	**MEK**	45	94 / 6
12	40	**Toluene**	46	94 / 6
13	40	**Acetonitrile**	0	-
14	40	**Hexane**	3	99 / 1

a) Reaction conditions: $Rh_6(CO)_{16}$ (0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), solvent (5 ml), 600 psi (CO/H_2 = 1/1), 16 h.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^1H NMR.

obtained with the system $Rh_6(CO)_{16}$/ HPA-W_{12} at 40-45 ^oC, where the total conversion and the highest selectivity of the reaction were achieved.

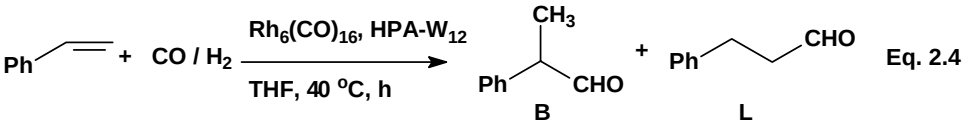
The study of the effect of changing the type of solvent on the hydroformylation of styrene by the catalytic system $Rh_6(CO)_{16}$/ HPA-W_{12} is shown in Table 2.2 entries 8-14. Among the tested solvents, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), 1,4-dioxane, and dichloromethane (CH_2Cl_2) gave conversions of 97 %, 92 %, 88 %, and 84 %, respectively (Table 2.2, entries 7-10). MEK and toluene gave average conversions (45 % and 46 %). The catalytic system with other solvents such as acetonitrile and hexane gave traces or no reaction at 40 ^oC for 16 h. It seems that the catalytic system showed higher catalytic activity in polar solvent than in non-polar solvent. This can be explained by the catalytic active intermediate species, which is more stable in THF and other polar solvents.

2.3.4 Hydroformylation of Styrene catalyzed by $Rh_6(CO)_{16}$ / HPA-W_{12} Effect of the ratio of CO / H_2 and the Reaction Time

The effect of the ratio of CO / H_2 at constant total pressure of 600 psi was studied with the catalytic system $Rh_6(CO)_{16}$ / HPA-W_{12} (Table 2.3). An increase in the ratio of CO / H_2 from 1/1 to 4/2 and 5/1 decreased the conversions of styrene from 97 % to 75 % and 28 %, respectively (Table 2.3, entries 1-3). However, the decrease of the ratio of CO / H_2 to 2/4 and 1/5 maintained the conversions relatively high (92 % and 88 %) with slight drop in the selectivity in the branched aldehyde **B** (Table 2.3, entries 4,5). No products were obtained in the absence of hydrogen (Table 2.3, entry 6).

The study of the conversions of the reaction of the hydroformylation of styrene at different times with the catalytic system $Rh_6(CO)_{16}$/HPA-W_{12} is summarized in Table

Table 2.3 Hydroformylation of Styrene catalyzed by $Rh_6(CO)_{16}$ / HPA-W_{12}. Effect of CO / H_2 pressure and the reaction time.[a]



Entry	**Time h**	**Pressure CO / H_2 Psi**	**Conversion[b] %**	**Product Distribution[c] % B / L**
1	**16**	**300 / 300**	95	94 / 6
2	16	**400 / 200**	75	92 / 8
3	16	**500 / 100**	28	93 / 7
4	16	**200 / 400**	92	89 / 11
5	16	**100 / 500**	88	84 / 16
6	16	**600 / 0**	0	-
7	**3**	300 / 300	28	94 / 6
8	**6**	300 / 300	34	93 / 7
9	**9**	300 / 300	70	92 / 8
10	**12**	300 / 300	82	93 / 7

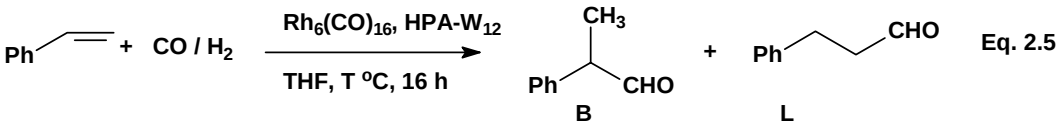
a) Reaction conditions: $Rh_6(CO)_{16}$ (0.0011g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (5.0 mmol), THF 5 ml, 40 °C.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^{1}H NMR.

2.3, entries 7-10. Low conversions after 3-6 h (28-34 %) and good conversions after 9-12 h (70-82 %) were obtained. The results indicated clearly that the kinetics of the reaction is slow with this catalytic system. However, the rate of the reaction can be improved significantly by increasing the temperature of the reaction to 80 ^{o}C or 100 ^{o}C, but the selectivity of the reaction toward **B (XXIII)** dropped after 6 h of the reaction from 94 % to 72 %. It seems clearly that the advantage of the slower reaction is to maintain both high conversions and high selectivity of products.

2.3.5 Hydroformylation of Styrene catalyzed by $Rh_6(CO)_{16}$. The improvement of the reaction time and the selectivity.

The reaction of hydroformylation of styrene by $Rh_6(CO)_{16}$ at 40 ^{o}C suffers from the relatively prolonged time for the completion of the reaction. The reaction time was improved significantly by increasing the reaction temperature to 60 ^{o}C. However, the selectivity was affected by the change in the conditions of the reaction. We have studied the effect of the temperature and the addition of a ligand for the objective of improving the reaction time and maintaining the selectivity and the conversion of the reaction relatively high. The effect of the reaction temperature on the reaction time has been studied carefully by considering a wide range of temperatures (25-80 ^{o}C) and in the presence of the catalyst system $Rh_6(CO)_{16}$-HPA-W_{12} in THF as a solvent (Table 2.4). The results of the reaction after 6 hours showed very low conversion (5-20 %) at temperatures (25-40 ^{o}C) (Table 2.4, entries 1-2). The conversion increased to 47 % and further to 94 % at 50 ^{o}C and 60 ^{o}C, respectively (Table 2.4, entries 3, 5). In the absence HPA-W_{12}, the conversions of styrene were lower (37 % and 58 %) at 50 ^{o}C and 60 ^{o}C, respectively (Table 2.4, entries 4, 7). The conversion after 3 h of reaction, by using $Rh_6(CO)_{16}$-HPA-

Table 2.4 Hydroformylation of Styrene by $Rh_6(CO)_{16}$-HPA-W_{12}. Effect of the Temperature.[a]



Entry	T °C	Conversion[b] %	Product Distribution[c] % B / L
1	**25**	5	98 / 2
2	**40**	20	92 / 8
3	**50**	47	92 / 8
4[d]	**50**	35	95 / 5
5	**60**	94	88 / 12
6[e]	**60**	69	89 / 11
7[d]	**60**	58	90 / 10
8[e]	**80**	98	73 / 27
9[f]	**60**	96	93 / 7

a) Reaction conditions: $Rh_6(CO)_{16}$ (0.001 mmol, 0.001 g), HPA-W_{12} (0.010 mmol = 0.0333 g), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO/H_2=1/1), 6 h.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^{1}H NMR.
d) No HPA-W_{12} was used
e) Reaction time = 3 h.
f) $P(OPh)_3$ (0.020 mmol) in place of HPA-W_{12}

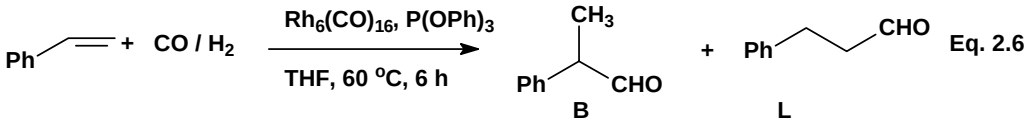
W_{12} as catalytic system, dropped to 69 % at 60 ^{o}C (Table 2.4, entry 6). The increase of the temperature to 80 ^{o}C led to almost total conversion (98 %) of styrene after 3 h but the selectivity toward the branched aldehyde dropped to 73 % (Table 2.4, entry 8). The most interesting result was observed when HPA-W_{12} was replaced by the phosphite ligand $P(OPh)_3$ (Table 2.4, entry 9). The conversion was maintained excellent (96 %) and the selectivity toward the branched aldehyde was also extremely high (93 %) after 6 h of reaction. The role of the heteropolyacid is most probably in increasing the solubility of the rhodium cluster and also in forming relatively stable catalytic intermediates in THF *via* Rh-W bonding system within the heteropolyacid moiety.

2.3.6 Effect of the amount of phosphite ligand on the selectivity and the reaction time.

The preliminary interesting results obtained with the phosphite led us to explore this important ligand and to optimize the reaction conditions toward maximum conversion and selectivity. The results on Figure 2.1 showed excellent conversions and selectivities with the amount of triphenyl phosphite ranged from 0.01 to 0.05 mmol at 60 ^{o}C and 6 h. The addition of higher amount of phosphite (>0.06 mmol) decreased the conversion of styrene in a significant manner and the reaction was almost totally inhibited at >1.0 mmol of phosphite.

It appears that the best conversion and selectivity were obtained with 0.02 mmol of $P(OPh)_3$ with the ligand to catalyst ratio equals to 20. The optimal ratio of the substrate to catalyst (styrene / $Rh_6(CO)_{16}$) was 5000. We believe that a very active species such as $Rh(CO)_x(OPh)_y$ was formed in situ where the use of a large excess of phosphite stabilizes probably the intermediate $Rh(OPh_3)_z$ with is not catalytically very active.

Hydroformylation of Styrene catalyzed by $Rh_6(CO)_{16}$. Effect of the amount of $P(OPh)_3$.



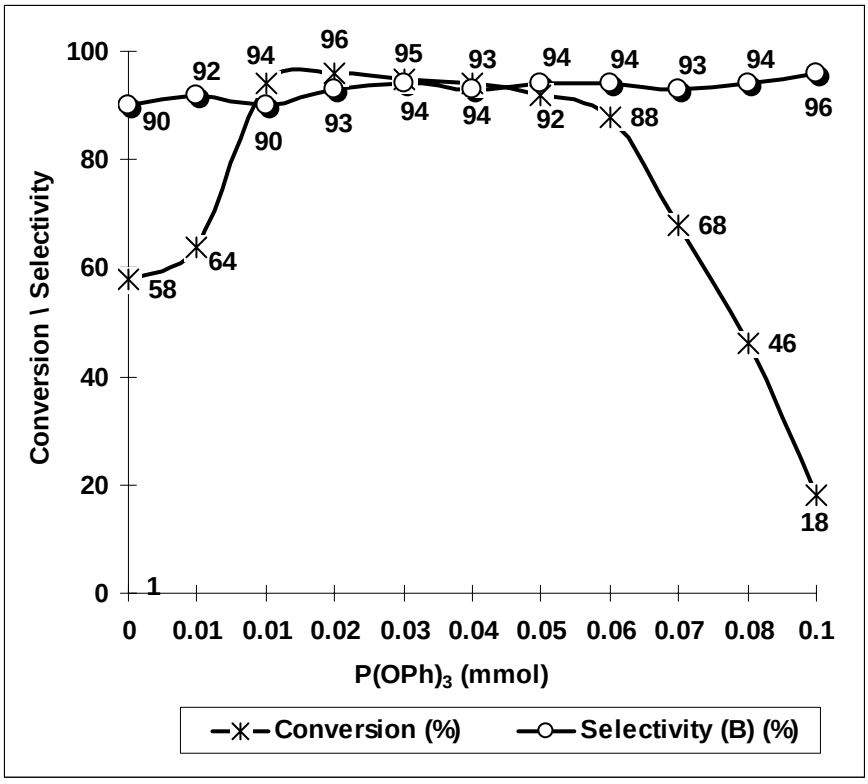


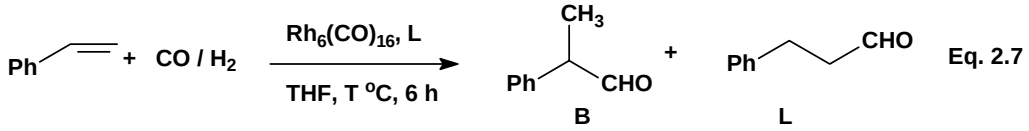
Figure 2.1
Reaction conditions: $Rh_6(CO)_{16}$ (0.001 mmol), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO/H_2=1/1), 60 °C, 6 h.

2.3.7 Effect of the temperature and type of ligands on the activity and selectivity.

The temperature has also an important role in the reaction catalyzed by $Rh_6(CO_{16}$–$P(OPh)_3$ (Table 2.5). Low conversions were observed at temperature below 60 ^oC (Table 2.5, entries 1, 2). The conversion increased from 48 % at 50 ^oC to 96 % at 60 ^oC with the selectivity toward the branched aldehyde maintained high after 6 h of reaction (Table 2.5, entry 3). At 60 ^oC and after only 3 h, the conversion dropped to 68 % (Table 2.5, entry 4). At higher temperature (80 ^oC), the maximum conversion was obtained after 3 hours of the reaction but the selectivity toward the branched aldehyde dropped to 81% (Table 2.5, entry 5). In summary at lower temperatures, longer reaction is needed for the total conversion of styrene and at high temperatures a serious loss in the selectivity of the reaction was observed.

Other phosphine ligands have been considered in the reaction of the hydroformylation of styrene during the optimization process (Table 2.5). Most of monophosphines such as PPh_3, PCy_3, and PBu_3 and also the diphospine ligands (Table 2.5, entries 3-6) gave very low conversion (2-10 %). PPh_3 is the only monophosphine that gave better conversion 45 % (Table 2.5, entry 2). It was very obvious that the triphenyl phosphite was by far the most active ligand among the many tested ligands for this reaction. Maximum conversion (96 %) and selectivity (93 %) were obtained in THF as a solvent and with $Rh_6(CO)_{16}$ as a catalyst. The diphosphine ligands form probably very stable and non-active intermediates [**P-Rh-P]** in THF for the hydroformylation of styrene.

Table 2.5 Hydroformylation of Styrene by $Rh_6(CO)_{16}/P(OPh)_3$: Effect of temperature and type of ligand.[a]



Entry	T °C	Ligand	Conversion[b] %	Product Distribution[c] % B / L
1	**40**	$P(OPh)_3$	29	95 / 5
2	**50**	$P(OPh)_3$	48	94 / 6
3	**60**	**$P(OPh)_3$**	96	93 / 7
4[d]	**60**	$P(OPh)_3$	68	94 / 6
5[d]	**80**	$P(OPh)_3$	98	81 / 19
6	60	**PPh_3**	45	92 / 8
7	60	**PCy_3**	9	99 / 1
8	60	**PBu_3**	10	98 / 2
9	60	**dppb**	2	99 / 1
10	60	**dppp**	Traces	-

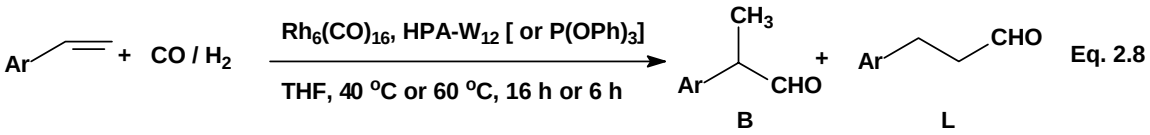
a) Reaction conditions: $Rh_6(CO)_{16}$ (0.001 mmol), ligand (0.020 mmol = 0.0062g), styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO/H_2 = 1/1), 6 h.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^1H NMR.
d) Reaction time = 3 h.

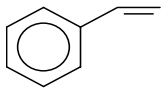
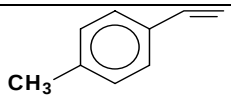
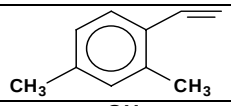
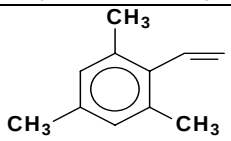
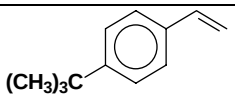
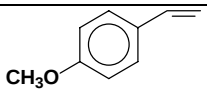
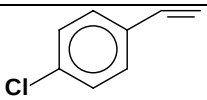
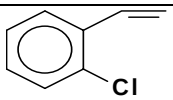
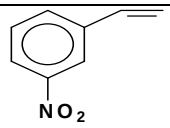
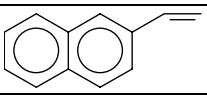
2.3.8 Hydroformylation of various aryl alkenes by $Rh_6(CO)_{16}$ / HPA-W_{12} [or $P(OPh)_3$] / CO / H_2 / THF

The hydroformylation of different styrene derivatives was achieved with high conversions and selectivities with the catalytic systems $Rh_6(CO)_{16}$/HPA-W_{12}/CO/H_2/40°C/16h (**system A**) and $Rh_6(CO)_{16}$/$P(OPh)_3$/CO/H_2/60°C/6h (**system B**) in THF as a solvent (Eq. 2.8) (Table 2.6). The main differences between the two catalytic systems are the ligand, temperature and reaction time. The two systems **A** and **B** gave very similar results in terms of conversions and selectivities. The presence of a methyl group, two methyl groups or three methyl groups substituted on the benzene ring did not affect the reactivity in terms of conversions of the styrene derivatives and selectivities of branched aldehydes **B** (Table 2.6, entries 3-8). However, the *p*-methoxystyrene gave excellent conversion and selectivity in the presence of $H_3PMo_{12}O_{40}$ (HPA-Mo_{12}) (Table 2.6, entry 11) in place of HPA-W_{12}, because we have observed that important part of *p*-methoxystyrene were polymerized with HPA-W_{12} and not with HPA-Mo_{12}. 2-chloro-, 4-chloro, and 2-naphthylstyrene were also very reactive substrates and led to excellent conversions and selectivities of the reactions (Table 2.6, entries 13-16, 19-20). 3-nitrostyrene undergoes also the hydroformylation with relatively good conversion (64 %) and selectivity toward the corresponding branched aldehyde **B** (86 %) (Table 2.6, entries 17,18).

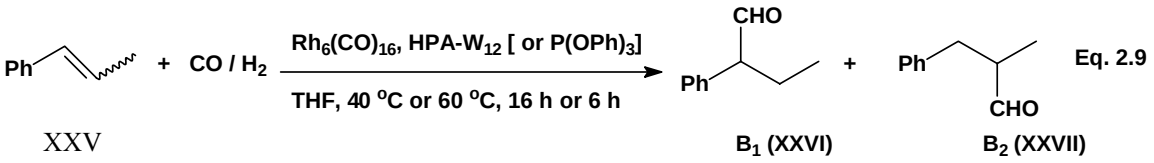
β-Methylstyrene (XXV) reacted under the conditions of catalytic system **A** and gave a low conversion (37 %) of styrene and forming two branched aldehydes $\mathbf{B_1}$ (XXVI) and $\mathbf{B_2}$ (XXVIII) with a ratio of 78 / 22 (Eq. 2.9). The catalytic system **B** showed better activity than **A**; the conversion of styrene was about 65 % after 16 h and the selectivity toward the branched isomer $\mathbf{B_1}$ was also higher (84 %).

Table 2.6 Hydroformylation of various aryl alkenes by $Rh_6(CO)_{16}$/HPA-W_{12} or [$P(OPh)_3$] /CO/H_2/THF.[a]



Entry	Substrates	T°C / Time	Ligand	Conversion[b] %	Product Distribution[c] % B / L
1		40°C/16h	HPA-W_{12}	97	94 / 6
2		60°C/6h	$P(OPh)_3$	96	93 / 7
3		40°C/16h	HPA-W_{12}	96	93 / 7
4		60°C/6h	$P(OPh)_3$	97	94 / 6
5		40°C/16h	HPA-W_{12}	95	92 / 8
6		60°C/6h	$P(OPh)_3$	96	94 / 6
7		40°C/16h	HPA-W_{12}	95	92 / 8
8		60°C/6h	$P(OPh)_3$	97	93 / 7
9		40°C/16h	HPA-W_{12}	97	93 / 7
10		60°C/6h	$P(OPh)_3$	98	95 / 5
11[d]		40°C/16h	HPA-W_{12}	96	93 / 7
12		60°C/6h	$P(OPh)_3$	97	94 / 6
13		40°C/16h	HPA-W_{12}	98	95 / 5
14		60°C/6h	$P(OPh)_3$	99	96 / 4
15		40°C/16h	HPA-W_{12}	96	93 / 7
16		60°C/6h	$P(OPh)_3$	97	94 / 6
17		40°C/16h	HPA-W_{12}	64	86 / 14
18		60°C/6h	$P(OPh)_3$	86	90 / 10
19		40°C/16h	HPA-W_{12}	98	93 / 7
20		60°C/6h	$P(OPh)_3$	99	94 / 6

a. Reaction conditions: $Rh_6(CO)_{16}$ (0.0011g = 0.010 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g) or $P(OPh)_3$ (0.020 mmol = 0.0062 g), styrene (5.0 mmol), THF (5 ml), 600 psi (CO/H_2 = 1/1).
b. Determined by GC using anisole as internal standard.
c. Determined by GC and ^1H NMR.
d. $H_3PMo_{12}O_{40}$ (HPA-Mo_{12}) was used in place of HPA-W_{12}.



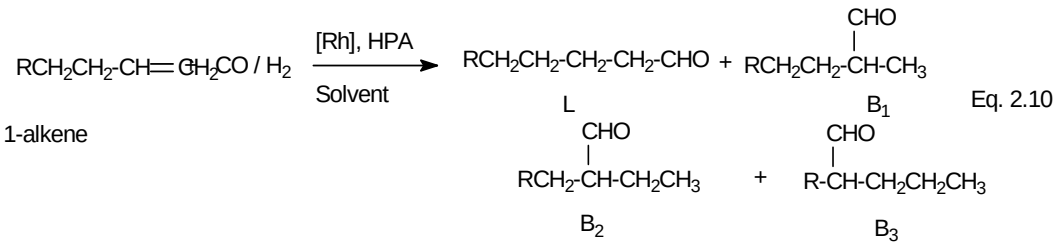
System		
A	78	22
B	84	16

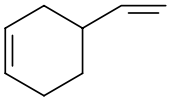
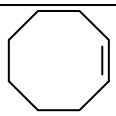
It seems that the catalytic systems $Rh_6(CO)_{16}$/HPA-W_{12}/CO/H_2/40°C/16h (**system A**) and $Rh_6(CO)_{16}$/$P(OPh)_3$/CO/H_2/60°C/6h (**system B**) in THF are efficient homogeneous systems for the hydroformylation of styrene derivatives at low temperature leading to excellent conversions of alkenes and excellent selectivities toward branched aldehydes.

2.3.9 Hydroformylation of various Terminal Alkyl Alkenes

The hydroformylation of different terminal alkyl alkenes was carried out by the catalytic system formed of $Rh_6(CO)_{16}$/HPA-W_{12}/CO/H_2 in THF (Table 2.10). We have observed that the alkene with short alkyl chain, such as 1-heptene, was less reactive than 1-octene. At 50 °C the conversion of 1-heptene was only 46 % compared to 66 % and 86 % at 60 °C and 80 °C, respectively (Table 2.7, entries 1-3). 1-dodecene was as reactive as 1-octene; the conversion of 1-dodecene was 75 % at 40 °C, 85 % at 50 °C and 91 % at 60 °C (Table 2.7, entries 5-7). 1-Tetradecene undergoes also the hydroformylation reaction with relatively high conversion (78 %) at 60 °C (Table 2.7, entry 8). Interestingly, we have observed that the process of isomerization of alkene was function of temperature and the length of alkyl chain of the alkene. For example, at 50 °C the unreacted alkenes for 1-heptene, 1-octene, and 1-dodecene at the end of the reaction were detected as follow: 83 % as 1-heptene (17 % other heptene isomers), 72 % as 1-octene (28 % other octene

Table 2.7 Hydroformylation of various Terminal Alkyl Alkenes by $Rh_6(CO)_{16}$/HPA-W_{12} /CO/H_2/THF.[a]



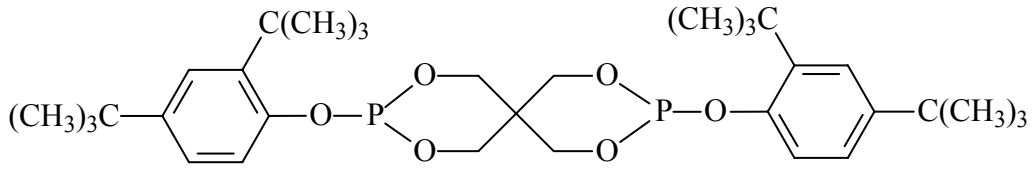
Entry	Substrate	T °C	Conv.[b] %	Product Distribution[c] %		Alkene[b] %
				B_1 / L	Isomers B_2+B_3+B_4	1-Alkene
1	**1-Heptene**	50	46	42 / 58	0	83
2	**1-Heptene**	60	66	69 / 61	0	68
3	**1-Heptene**	80	86	34 / 66	0	56
4	**1-Octene**	50	94	42 / 52	6	72
5	**1-Dodecene**	40	75	41 / 59	0	82
6	**1-Dodecene**	50	85	39 / 50	11	59
7	**1-Dodecene**	60	91	38 / 49	13	54
8	**1-Tetradecene**	60	78	38 / 50	12	45
9		60	87	26 / 74	-	-
10		80	58	100 / 0	-	-

a) Reaction conditions: $Rh_6(CO)_{16}$ (0.0011 g = 0.001 mmol), HPA-W_{12} (0.010 mmol = 0.0333 g), 1-octene (5.0 mmol), THF (5 ml), 16 h.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^{1}H NMR.

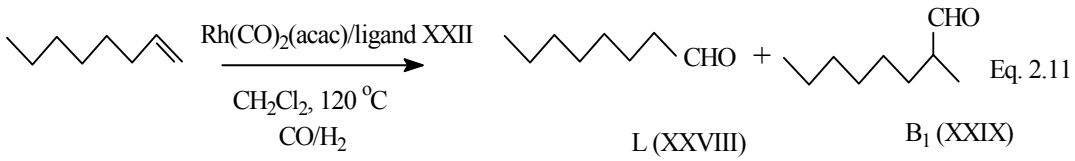
isomers) and 59 % as 1-dodecene (41 % other dodecene isomers). The effect of the temperature on the isomerization of 1-alkyl alkenes was clear with 1-heptene as a substrate, where the percentage of unreacted 1-heptene was 83 % at 50 ^{o}C, 6 8% at 60 ^{o}C.

2.3.10 Hydroformylation of 1-octene catalyzed by $Rh(CO)_2(acac)$-Bulky phosphite (XXII). Effect of Temperature and Solvent

Hydroformylation of 1-octene, chosen as a model substrate, into nonanal (**L** or n) and 2-methyl octanal (**B_1** or i) occurred smoothly at relatively mild conditions [120 ^{o}C, 300 psi (CO/H_2= 1:2), 60 minutes], with $Rh(CO)_2(acac)$ used as catalyst and XXII used as a ligand (Eq. 2.11).



bis(2,4-di-terbutylphenyl)pentaerythritol diphosphite (XXII)



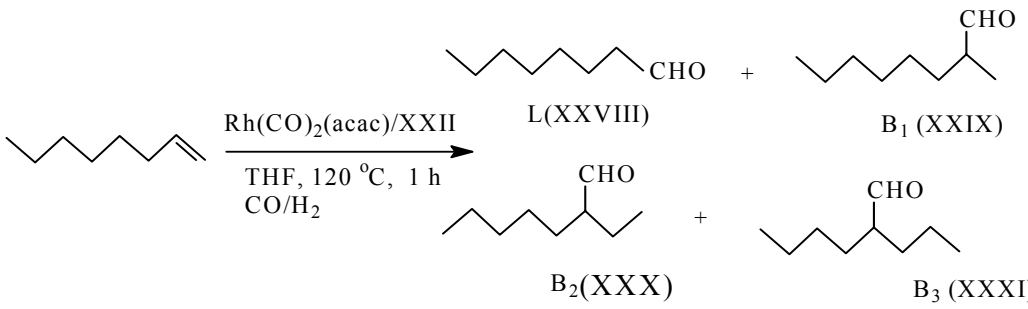
Eq. 2.11

The change of the temperature has a major effect on the distribution of the products due to the competitive reactions including the hydroformylation / isomerization of the double bonds and the dissociation of ligand from the catalytic complexes at higher temperature (2). A systematic study on the influence of the temperature on the regioselectivity and the catalytic activity in the hydroformylation of 1-octene in dichlomethane as a solvent was carried out at a variety of temperatures ranging from 80

^{o}C to 130 ^{o}C. The results are shown on Table 2.8. The formation of the linear aldehyde prevailed in all cases at all temperatures.

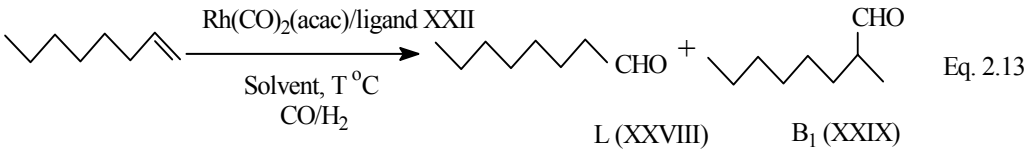
The results of the reaction after 1 hour showed a very low conversion (17 %) at 80 ^{o}C (Table 2.8, entry 4) with n / i ratio of 5.8. The conversion increased to 68 % and further to 72 % at 100 ^{o}C and 120 ^{o}C with the increase of the corresponding n / i ratio of 6.7 and 19, respectively (Table 2.8, entries 3,2). Higher temperature (130 ^{o}C) led to a higher conversion (78 %) of 1-octene but the n / i ratio dropped to 13.3 (Table 2.8, entry 1).This drop of n / i ratio at 130 ^{o}C can be explained by the activation of the process of the isomerization of 1-octene into internal octenes that resulted in increasing the amount of branched aldehydes isomers, hence lower n / i ratio.

The study of the effect of the type of solvent on the hydroformylation of 1-octene by the catalytic system $Rh(CO)_2$ / XXII is also shown in Table 2.8 (entries 5-9). Among the tested solvents, toluene, DMSO, n-heptane, and propylene carbonate led to conversions of 87 %, 82 %, 66 %, and 59 %, with corresponding n/i ratio of 7.5, 13.3, 9.0, and 11.5 respectively (Table 2.8, entries 5-9). For THF, the selectivity in the linear isomer is 70 %, that of predominant branched isomer (2-methyl octanaldehydes) is 22 % and that of other branched isomers B_2, 2-ethyl heptanaldehydes (XXX) (Eq 2.13) is 8 % as shown in Table 2.8, entry 7.



Eq. 2.12

Table 2.8 Hydroformylation of 1-octene by $Rh(CO)_2(acac)$-XXII. Effect of the solvent and temperature.[a]



Eq. 2.13

Entry	T °C	Solvent Ml	CO/H_2 psi	Conv. [b] %	B/L[c]	n/i	% 1-octene
1	**130**	CH_2Cl_2	100/200	78	7/93	13.3	9
2	**120**	CH_2Cl_2	100/200	72	5/95	19	9
3	**100**	CH_2Cl_2	100/200	68	13/87	6.7	83
4	**80**	CH_2Cl_2	100/200	17	16/84	5.3	99
5	120	**Toluene**	100/200	87	12/88	7.3	31
6	120	**DMSO**	100/200	82	7/93	13.3	49
7	120	**THF**	100/200	77	30/70[d]	2.3	4
8	120	**n-heptane**	100/200	66	10/90	9	69
9	120	**Propylene carbonate**	100/200	59	8/92	11.5	83

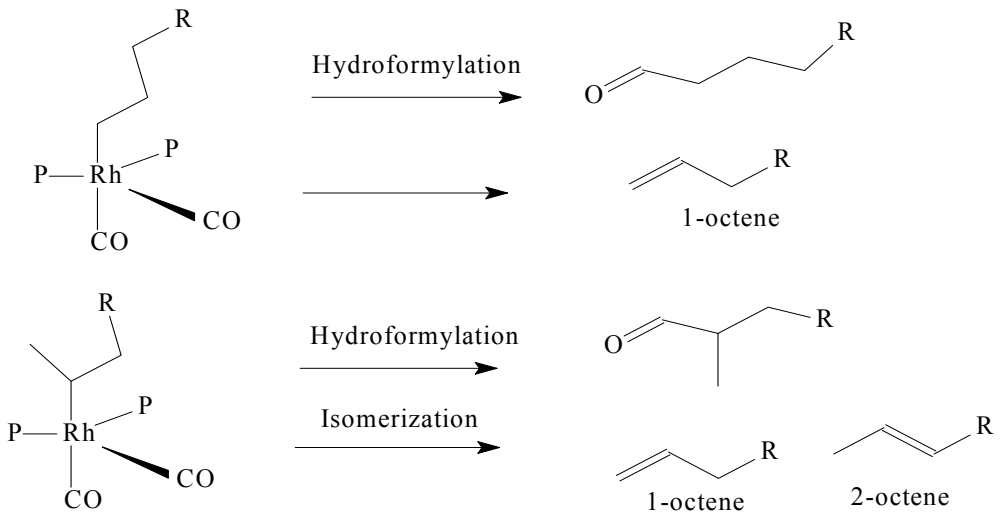
a) Reaction conditions: **$Rh(CO)_2(acac)$** (0.005mmol), 1-octene (5.0 mmol), Solvent (5 ml), 100/200 (CO/H_2 = 1/2), 120 °C, 0.03 mmol XXII.
b) Determined by GC.
c) Determined by GC and ^1H NMR.
d) Branched B_1+ B_2 (B_1 = 22, B_2 = 8).

2.3.11 Hydroformylation of 1-octene catalyzed by $Rh(CO)_2(acac)$-XXII. Effect of CO / H_2 pressure and reaction time

The effect of the ratio of CO / H_2 was studied with the catalytic system $Rh(CO)_2(acac)$ / XXII (Table 2.9). At the total pressure of 300 psi of CO / H_2, the conversion increases from 62 % for CO / H_2 = 1/5 to 72 % for CO / H_2 = 1/2 and finally to 90 % for CO / H_2 2/1. The ratio decreases from 24 at the ratio of CO / H_2 1/5, to 19 at 1/2 and finally to 5.3 at 2/1. The percentage of the non-isomerized starting material (1-octene) increases with the increase in CO partial pressure (Table 2.9, entries 1-4). Similar observation were made with the total pressure of 600 psi: decreasing the partial pressure of CO from 500 (CO/ H_2 = 5/1) to 300 (CO/ H_2 = 1/1), and 100 psi (CO / H_2 = 1/5) maintains the conversions of 1-octene relatively high (92, 87, and 87 %, respectively), with the decrease in n / i ratio from 3.8, to 5.3, and finally to 9, respectively (Table 2.9, entries 7-9). No products were obtained in the absence of hydrogen.

The negative dependence of n / i ratio on CO partial pressure can be explained as follow: isomerization of alkene occurs only when β-H elimination of the branched alkylrhodium compound takes place (Scheme 2.1). The β-H elimination of the linear alkylrhodium species reformed the 1-octene. This β-H elimination reaction, facilitated at low CO pressures, converts the branched alkylrhodium into the 2-octenes. Thus, at low pressures, a substantial amount of the branched alkylrhodium complex does not proceed to form the branched aldehydes and consequently (at the incomplete conversions) the n / i ratio of aldehydes increases. However, the decrease of the isomerization rate at high CO pressures cannot totally account for the loss of selectivity (Table 2.9, entries 4,7,8). The presence of rhodium complexes that contain only one or even no rhodium-phosphorous

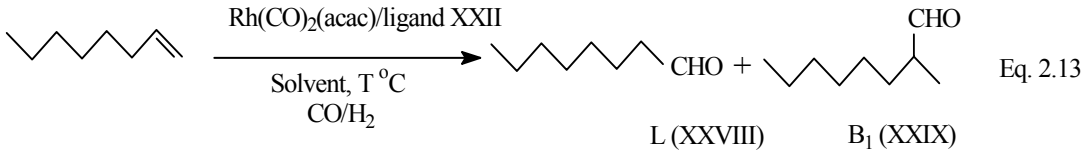
bonds can lead to this result, because these complexes are expected to react with low selectivity and high rate (92).



Scheme 2.1

The effect of varying the reaction time on the conversion and the selectivity in the catalytic hydroformylation of 1-octene was studied (Table 2.9). Generally, the conversion increases with the time. Moderate conversions were obtained after 1/4 h (64 %) and 1/2 h (72 %). The conversion increases to 85 % after 6 h. The n / i ratio increases steadily from 9 after 1/4 h to a maximum 19 after 1 h, then decreases to 4.7 after 6 h. Therefore, the optimum reaction time with respect to n / i ratio was 1 h; longer reaction time decreases the proportion of n-nonanal because of the isomerization of 1-octene to the internal octenes, hence increasing the branched isomer (6). The initial lower value for n / i ratio was obtained due probably to the slow rate of coordination of the ligand to the rhodium center.

Table 2.9. Hydroformylation of 1-octene by $Rh(CO)_2(acac)$-XXII. Effect of CO / H_2 pressure and reaction time.[a]



Eq. 2.13

Entry	T °C	Time H	CO/H_2 psi	Conv.[b] %	B/L[c]	n/i	1-octene %
1	120	1	**50/250**	62	4 / 96	24	5
2	120	1	**100/200**	72	5 / 95	19	9
3	120	1	**150/150**	81	11 / 89	8.1	16
4	120	1	**200/100**	90	16 / 84	5.3	50
5	120	1	**50+50/200**	66	6 / 94	16	5
6	120	1	**100/100**	68	6 / 94	16	7
7	120	1	**500/100**	87	21 / 79	3.8	67
8	120	1	**300/300**	92	16 / 84	5.3	25
9	120	1	**100/500**	87	10 / 90	9	12
10	120	**0.25**	100/200	64	10 / 90	9	71
11	120	**0.5**	100/200	72	6 / 94	15.7	13
12	120	**3**	100/200	74	6 / 94	16	6
13	120	**6**	100/200	85	17/ 82	4.7	13

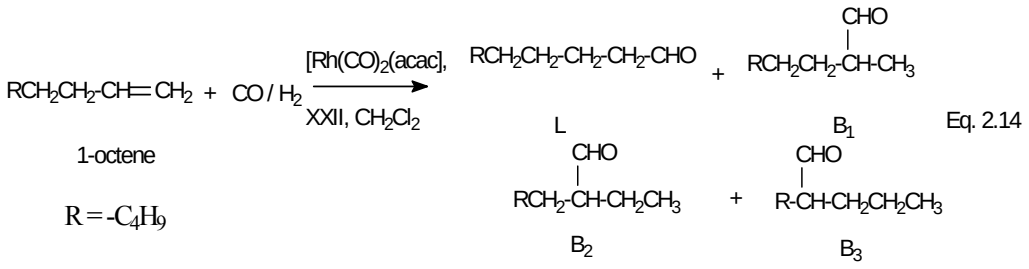
a) Reaction conditions: **$Rh(CO)_2(acac)$** (0.005mmol), 1-octene (5.0 mmol), CH_2Cl_2 (5 ml), 100/200 (CO/H_2 = 1/2), 120 °C, 0.03 mmol XXII.
b) Determined by GC.
c) Determined by GC and ^1H NMR.

2.3.12 Hydroformylation of 1-octene catalyzed by $Rh(CO)_2(acac)$-XXII. Effect of amount of ligand

Ligand XXII was applied in the rhodium-catalyzed hydroformylation of 1-octene. The catalyst was prepared in situ from $Rh(CO)_2(acac)$, the required amount of ligand, CO (100 psi) and H_2 (200 psi) at 120 ^oC, the results are shown in Figure 2.2. Very low conversion (23 %) and n / i ratio of aldehydes equals to 0.8 were obtained in the absence of the ligand XXII, due to the contribution of other side reactions such as hydrogenation and isomerization of 1-octene. Interestingly, the addition of 0.005 mmol of XXII (i.e. L / [Rh] = 1) has significantly improved the total conversion of aldehydes (53 %) with n / i ratio of 1.5. At a ratio of L / [Rh] of 6, a maximum n / i ratio of 19 was obtained at the conversion of 72 %. The further addition of XXII (L / [Rh] = 12) resulted in a decrease of the n / i ratio to 16. The total conversion dropped to 40 % with n / i ratio = 10.1 when the L / [Rh] was increased to 16. The negative dependency of the reaction rate on the ligand concentration can be explained by the formation of less active rhodium complexes (11, 93).

It has been found that a 10-fold amount of bulky diphosphite (XVIII) was required to reach a total conversion with Rh(COD)(acac) although only one phosphite ligand can coordinate to the rhodium center (92). Further addition of the diphosphite does not affect the rate of the reaction. Similarly, it was found that ligand-to-rhodium ratio of 5 is the minimum amount of ligand needed. The use of lower L / [Rh] resulted into the formation of a large amount of 2-octene (93).

Hydroformylation of 1-octene catalyzed by $Rh(CO)_2(acac)$ / XXII. Effect of the amount of XXII



Eq. 2.14

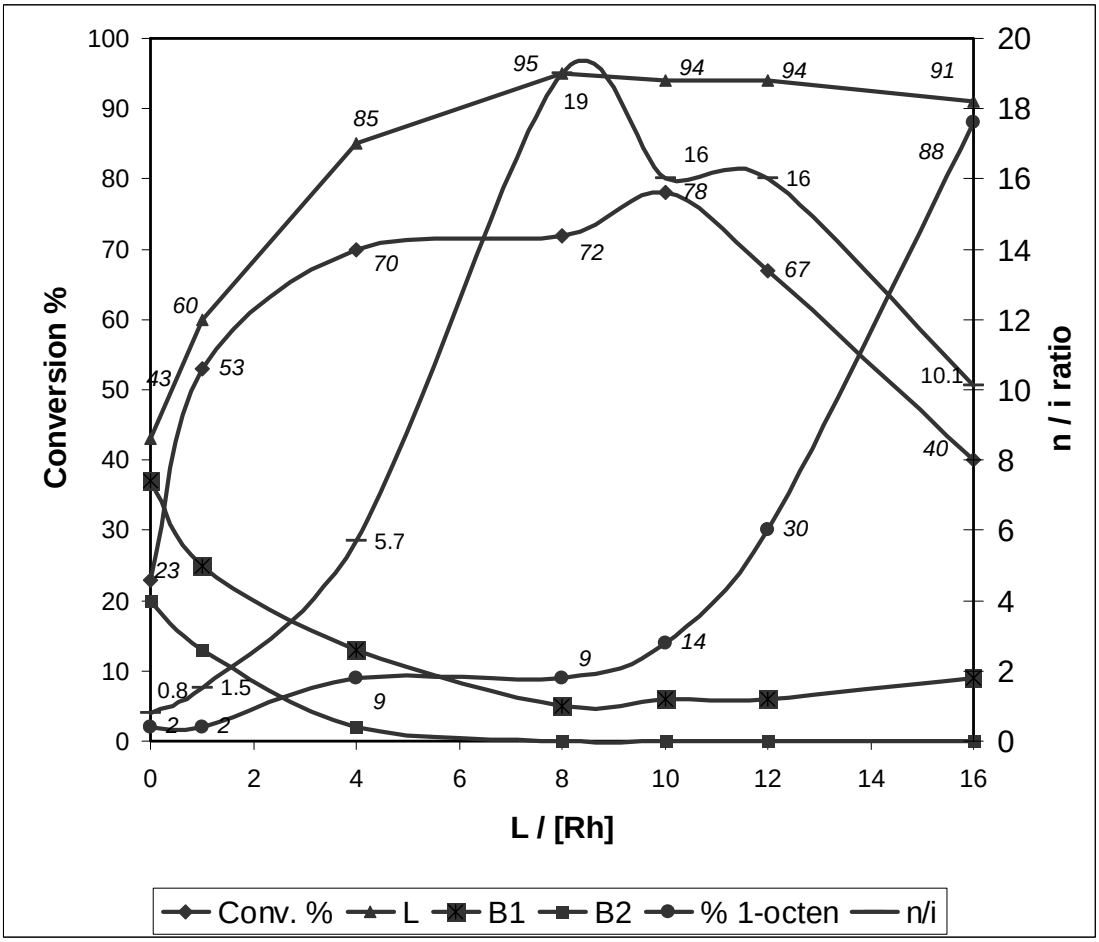


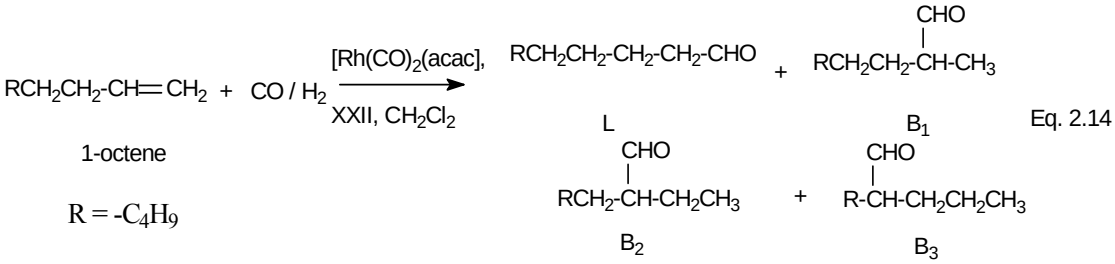
Figure 2.2
Reaction conditions: $Rh(CO)_2(acac)$ (0.00-0.08 mmol), 1-octene (0.56 g = 5.0 mmol), CH_2Cl_2 (5 ml), 300 psi (CO/H_2 = 1/2), 120 ^oC, 1 h.

2.3.13 Hydroformylation of 1-octene. Effect of the type of rhodium complex and other ligands.

The effect of the type of the rhodium catalyst in the reaction of hydroformylation of 1-octene was also studied in the presence of XXII. $RhCl_3.3H_2O$ showed a good catalytic activity in the conversion of 1-octene into aldehydes only after 16 h of reaction time, with the conversion of 72 % and n / i ratio of 10.1. While lower conversion (65) was obtained with $Rh_6(CO)_{16}$ after 1 h (Table 2.10, entry 2). The highest conversion (85 %) and the lowest n / i ratio (7.3) was obtained with $HRh(CO)(PPh_3)_3$. The results obtained showed that $Rh(CO)_2(acac)$ combined with XXII represents the most suitable catalytic system for the hydroformylation of 1-octene in dichloromethane as solvent.

Other phosphine ligands have been considered in the reaction of the hydroformylation of 1-octene during the optimization process (Table 2.10). Most of monophosphines such as PPh_3, $P(OPh)_3$, and 2,4-ditertbutyl triphenylphosphine gave good conversions (83, 69, and 70 %, respectively), but the selectivity for the linear aldehydes was very poor (n / i = 2.7, 3.2 and 0.7) because of the isomerization (Table 2.10, entry 10-13). In addition, the diphosphine ligands such as dppp and dppb (Table 2.10, entries 6,7) gave very low conversion (29 and 2 % respectively), while the TRIPHOS gave only traces of the products. The experimental results indicated that XXII was by far the most active among the tested ligands for this reaction. A maximum conversion (72 %) and selectivity (95 %) were obtained in CH_2Cl_2 as a solvent and with $Rh(CO)_2(acac)$ as a catalyst. The low activities of the diphosphine ligands are probably related to formation of very stable and inactive intermediates [**P-Rh-P]** in CH_2Cl_2 for the hydroformylation of 1-octene.

Table 2.10 Hydroformylation of 1-octene. Effect of type rhodium complex and ligand.[a]



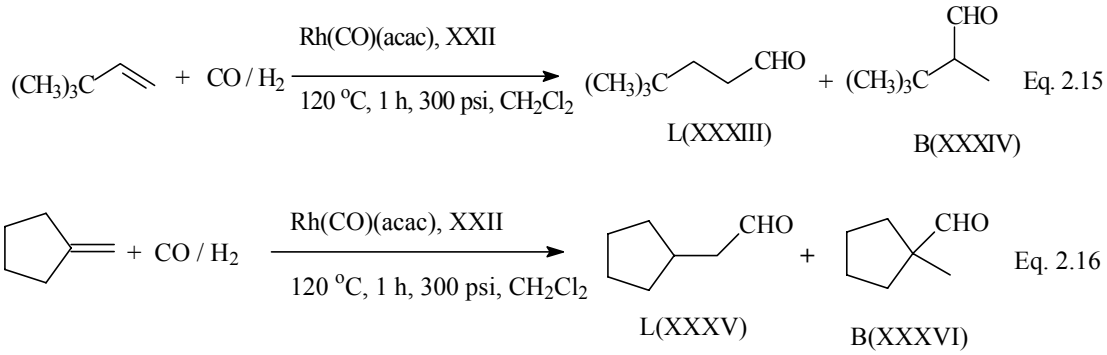
Eq. 2.14

Entry	Ligand or [Rh] Mmol	Conv. [b]%	L	B_1	B_2	L^c/ B_1+B_2	% 1-octene
1	**$Rh(CO)_2(acac)$**[c]	72	95	5	0	19	9
2	**$Rh_6(CO)_{16}$**[c]	65	89	11	0	8.1	68
3	**$HRh(CO)(PPh_3)_3$**[c]	85	88	12	0	7.3	12
4	**$RhCl(PPh_3)_3$**[c]	74	93	7	0	13.3	37
5	**$RhCl_3\ 3H_2O$**[c,d]	72	91	9	0	10.1	33
6	**dppp** (0.03)	29	75	25	0	3	63
7	**dppb** (0.03)	2	50	50	0	1	100
9	**Triphos** (0.02)	Traces	-	-	-	-	-
10	**PPh_3** (0.06)	83	73	25	2	2.7	9
11	**$P(OPh)_3$** (0.06)	69	76	8	6	3.2	4
12	**PBu_3** (0.06)	14	72	28	0	2.6	100
13	**P(2,4-di^{t}-BuPh)$_3$**	70	49	33	17	0.7	17

a) Reaction conditions: **$Rh(CO)_2(acac)$** (0.005mmol), 1-octene (5.0 mmol), CH_2Cl_2 (5 ml), 100/200 (CO/H_2 = 1/2), 120 ^oC.
b) Determined by GC and ^1H NMR.
c) Other [Rh] with 0.03 mmol of XXII. d) 16 h.

2.3.14 Hydroformylation of 1-octene catalyzed by $Rh(CO)_2(acac)$-XXII. Effect of different substrate

The hydroformylation of a variety of alkenes occurred smoothly at relatively mild conditions [120 ^oC, CO/H_2 (100/200 psi), 1.0h] with $Rh(CO)_2(acac)$ as a catalyst precursor and XXII as a ligand in dichloromethane (Table 2.11). For example, alkyl alkenes containing tertiary carbon atom bonded to the vinyl group, such as 3,3-dimethyl-1-butene, showed excellent regioselectivity toward the linear aldehyde. The main reason for such behavior was the steric effect, which prevents the addition of CHO moiety on the internal carbon of the double bond.



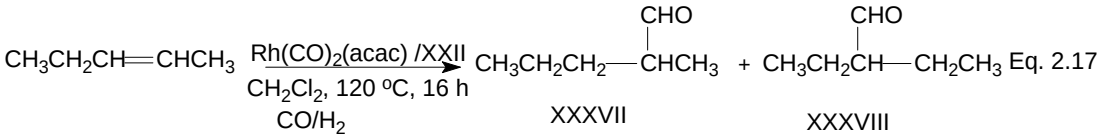
Similarly, methylene cylopentane was hydroformylated to give predominately the linear aldehyde, 2-cylopentyl ethanal **L (XXV)** (Appendix Figure A2.1), with only traces of the branched aldehyde, 1,1-cyclopentyl methyl methanal **B (XXVI)** (Eq. 2.16, Table 2.11, entry 8).

As expected, the hydroformylation of styrene occurred smoothly at the same experimental conditions in dichlomethane (Table 2.11, entry 1). The poor n / i ratio (0.8) is ascribed to a preference for a branched alkyl rhodium intermediate or electronically stabilized η^3-benzyl intermediate (92). The catalyst was also tested for the hydroformylation of internal alkene such as 2-pentene (Eq. 2.17) and β-methylstyrene

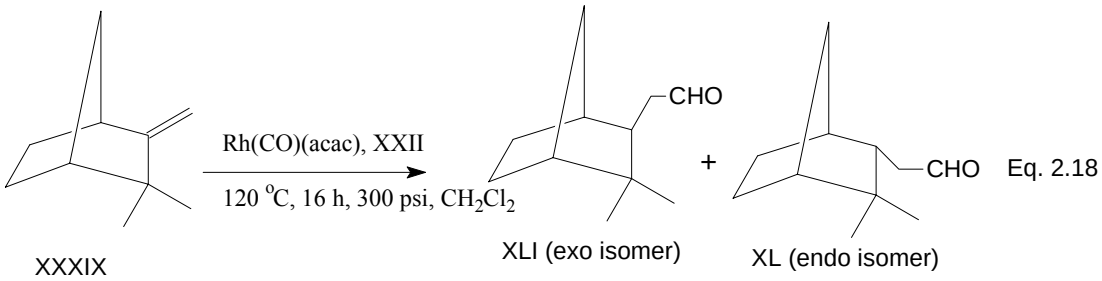
Table 2.11 Hydroformylation of different substrate catalyzed by $Rh(CO)_2(acac)$ / XXII.[a]

Entry	Substrate	Conv.[b] %	Isomer 1[c] %	Isomer 2[c] %	Isomer ratio
1	**Styrene**[d]	97	56 XXIII	44 XXIV	0.8
2	**2-pentene**	12	73 XXXVII	27 XXXVIII	2.7
3	**β-methylstyrene XXV**	21	76 XXVI	24 XXVII	3.2
4	**Cyclohexene**	65	$C_6H_{12}CHO$ 100	-	-
5	**3,3-dimethylbutene**	83	99 XXXIII	1 XXXIV	99
6	**Camphene XXXIX**	67	54 XL	46 XLI	1.2
7	**methylenecyclopetane**	80	90 XXXV	10 XXXVI	9

a) Reaction conditions: **$Rh(CO)_2(acac)$** (0.005mmol), Substrate (5.0 mmol), Solvent (5 ml), 100/200 (CO/H_2 = 1/2), 120 ^oC, 16 h, 0.03 mmol XXII.
b) Determined by GC.
c) Determined by GC and ^1H NMR.
d) 1 h



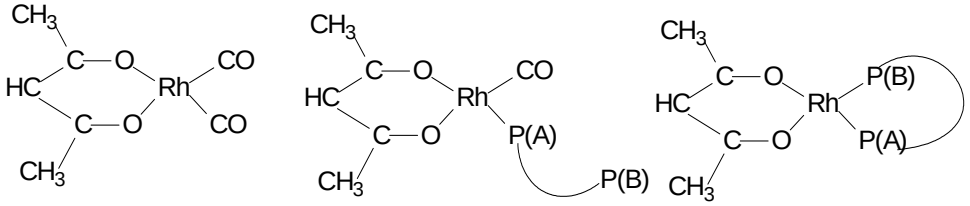
(Eq. 2.9) and showed a very low activity, with the conversions of 12 and 21 %, respectively after 16 h (Table 2.11, entry 2,3). Camphene (XXXIX) also undergoes the hydroformylation by the catalytic system ($Rh(CO)_2(acac)$ / XXII) to form the two aldehydes isomers XL (endo) and XLI (exo). A conversion of 67 % was achieved after 16 h. with a ratio of endo/exo of 1.2 (Eq. 2.18) (Appendix Figure A2.2).



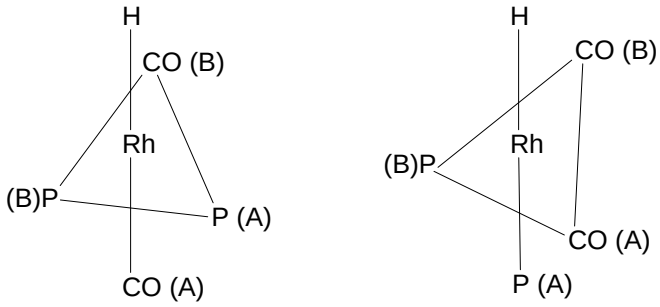
2.4 Mechanism

In order to identify the active catalyst complex and the possible intermediates during its formation, one equivalent of XXII was added to the $Rh(CO)_2(acac)$ (XLII) precursor. Immediately one CO ligand is substituted with the phosphorous ligand XLIII, this is concluded from the value of the single CO frequency of 2017 cm^{-1} compared the two germinal values of 2080 and 2008 cm^{-1} of the original precursor (Figure 2.3I, b,c). Also the upshift of its ^{31}P to δ 117 ppm the chemical shift of non-coordinating phosphorus, change slightly (δ = 12 ppm) compared to the free diphosphite ligand (δ = 7 ppm). After heating the mixture, the second CO ligand eventually was substituted. The IR

spectrum shows no CO absorptions in the region of 1600-2250 cm^{-1} (XLIV) (Figure 2.3I, d).



Under the syngas pressure, the rhodium acac precursors were converted to the catalytic active hydride complexes [RhH(XXII)$(CO)_2$]. The complexes are generally assumed to have a trigonal bipyramidal structure and two isomers of this structure are possible: the diphosphite coordinated in a bisequatorial **(ee)** or an equatorial-apical **(ea)** fashion. In the carbonyl region of the infrared spectrum the vibration of **ee** and **ea** can easily be distinguished. The **ee** complexes typically show absorptions around 2015 and 2075 cm^{-1} (92,93), where as **ea** complexes exhibit the carbonyl vibration around 1990 and 2030 cm^{-1} (93,94).



The IR spectrum obtained for hydroformylation reactions carried under various conditions (Figure 2.3II e,f,g) showed two absorption bands for the carbonyl ligands at 2069 and 2017 cm^{-1}, which lead to conclude that only equatorial-equatorial coordination **(ee)** isomer is present (95,96).

The reaction of 1-octene with the catalyst precursor (XLII) in the presence of 100 psi of CO resulted to the formation of a broad band around 1660 cm^{-1}, which is the region characteristic for the acyl group stretching (97), so it could be assigned to acyl complex (XLVII) (Figure 2.3Ia).

Additional bands are observed for $[Rh(XXII)(CO)_2]_2$ (XLVIII)complexes around 2066, 2045, 2017, 1844 cm^{-1} which become more intense when the corresponding ^{31}P NMR spectra show an increase in the degradation of ligand (Figure 2.3II, h). This can be explained by the displacement of the ligand resulting in the formation of carbonyl clusters. The IR spectroscopy studies on rhodium carbonyl compounds like $[Rh_4(CO)_{12}]$ has revealed band of 2080, 2050, 1860 cm^{-1} (98).

Following CO dissociation from the $HRh(CO)_2$(XXII) complexes, the regioselectivity in the hydroformylation will be determined by two consecutive steps of alkene coordination and hydride migration. van der Veen et. al (96) suggested that the regioselectivity is controlled by the alkene attack on the four-coordinate intermediate via a square-pyramidal transition state similar to structure XLIX (Scheme 2.2). Increasing bite angle of the diphosphite in intermediate XLIX results in increased embracing of the rhodium center by the ligand and consequently in more steric hindrance for the alkene entering the coordination sphere. The preference for the formation of the pro-linear over the pro-branched is not only determined by the magnitude of the bite angle, but also by the backbone constrains on the orientation of the phenyl substituent of the diphosphite in such a way that the formation of pro-linear is favored over the pro-branched.

The assumption that four-coordinate (L-L)Rh(CO)H complexes play a key role in the hydroformylation not only explains the effect of the bite angle on the regioselectivity but also explains the effect on the activity of the reaction. The natural bite angle

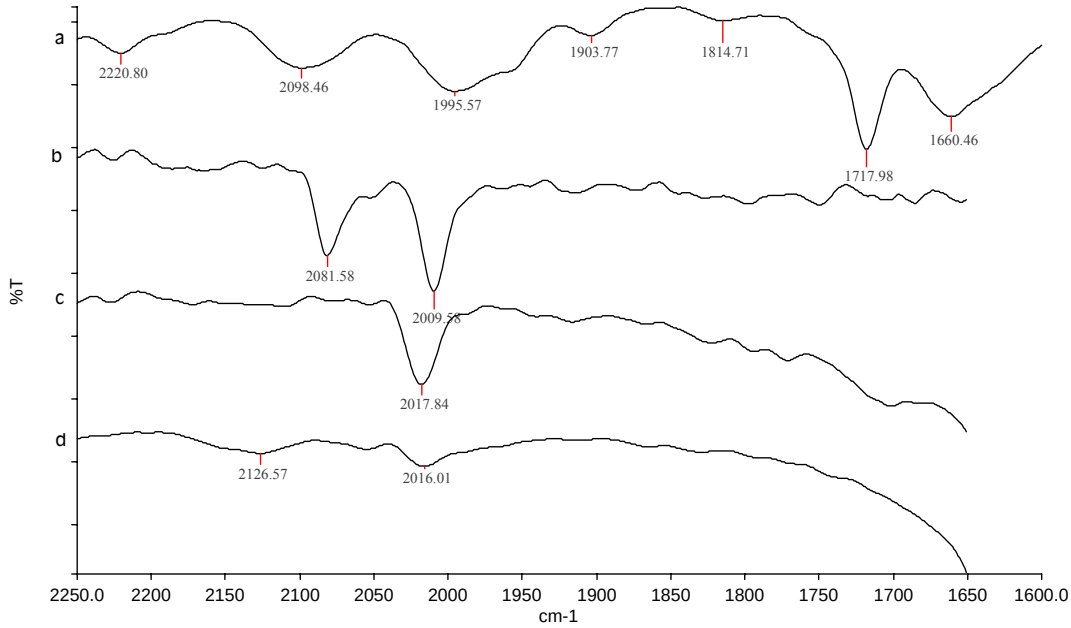


Figure 2.3I

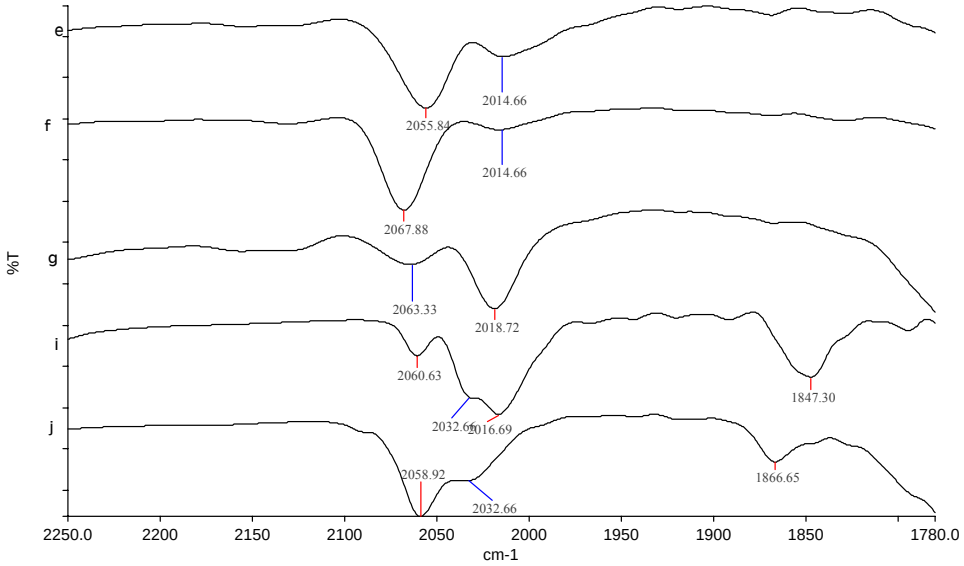
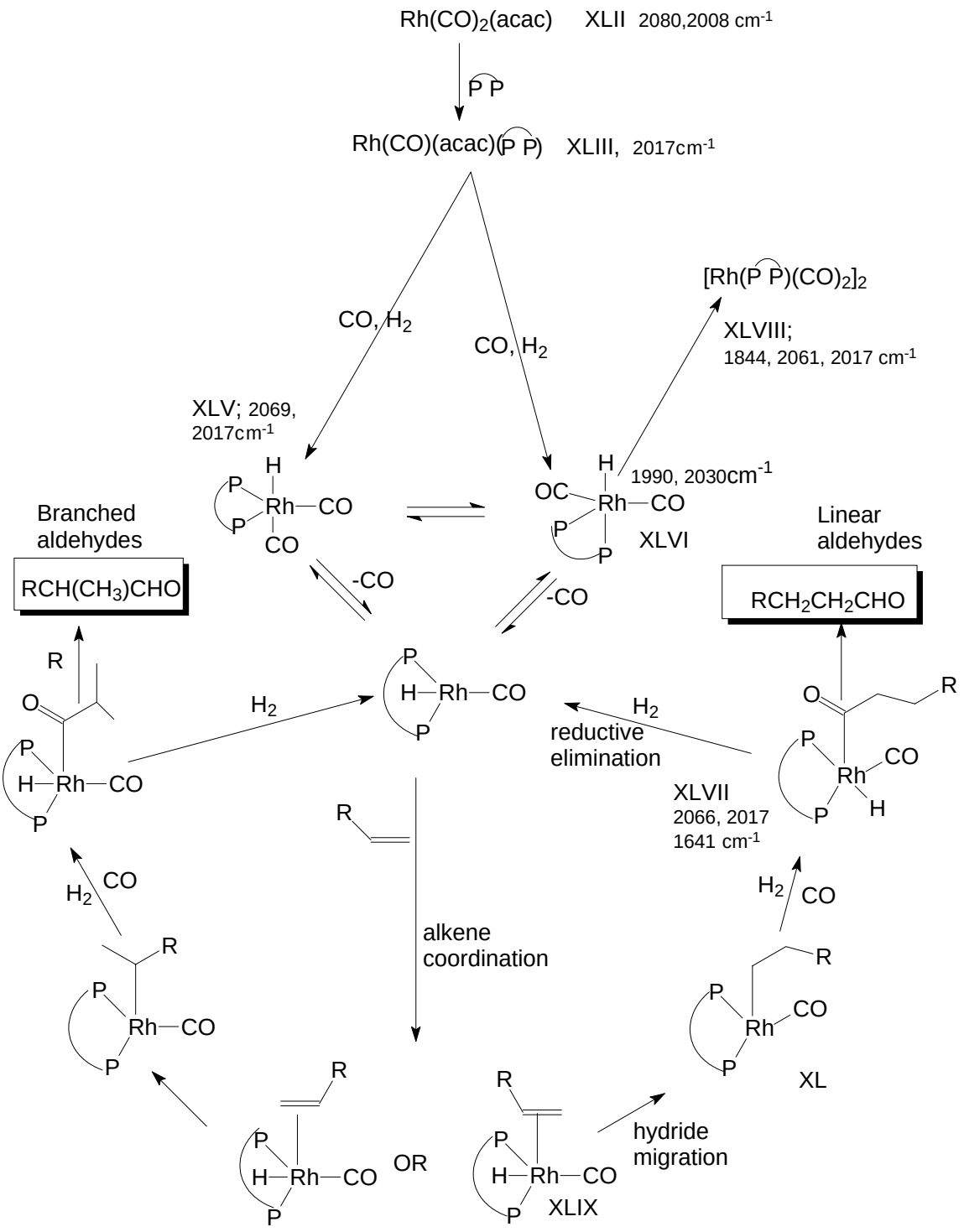


Figure 2.3II

FT-IR spectra of : a) the syntheses of acyl intermediate $Rh(CO)_2(acac)$ (0.01mmol), XXII (0.03 mmol), 1-octene (1.0 mmol), CO 200 psi, 1.5 ml CH_2Cl_2, 120°C, 1h; b) $Rh(CO)_2(acac)$ 0.01mmol, 1.5 ml CH_2Cl_2; c) same as b plus 0.01 mmol XXII; d) same as c after heating for 1/2h; e) $Rh(CO)_2(acac)$ (0.01mmol), XXII (0.03 mmol), 100/200 psi CO/H_2, 120°C, 1/2h; f) same as e plus 1.0 mmol 1-octene; g) same as f 500/100 psi CO/H_2; h) same as f with no ligand, i) same as f with 0.01mmol of XXII ligand.

Proposed reaction mechanism for the catalytic system $Rh(CO)_2(acac)$ / XXII



Scheme 2.2

influences the stabilities of the transient four-coordinate complexes and thus the activity of these intermediates. A diphosphite with natural bite angle close to 90^o cannot form a *trans* square-planer complex but will give an energetically less favorable cis complex (99). A higher stability of the transient four-coordinate (L-L)Rh(CO)H intermediate can result in a higher concentration of the intermediate and / or lower activation energy for its formation. If the decrease in activation energy for CO dissociation is accompanied by only a small increase in activation energy for alkene coordination to the four-coordinate complex, then both the higher reactant concentration and the lower activation energy can explain the observed increased in hydroformylation activity with increasing bite natural angle (100,101).

2.5 Conclusion

The results of the study showed clearly that the homogeneous catalytic system including $Rh_6(CO)_{16}$/HPA-W_{12}/CO/H_2/40^oC/16h (**system A**) and $Rh_6(CO)_{16}$/$P(OPh)_3$/CO/H_2/ 60^oC/6h (**system B**) in THF were active systems in the hydroformylation of styrene derivatives and alkyl alkenes. Excellent conversions of alkenes were observed. The role of the heteropolyacid HPA-W_{12} is probably through the formation of Rh-W-HPA intermediates and also in the formation and stabilization of the active rhodium carbonyl intermediate species at low temperature. The use of triphenyl phosphite **$P(OPh)_3$** was significant in terms of the improvement of the selectivity of the reaction. $P(OPh)_3$ is probably the most active ligand because it forms the active complex intermediates $Rh(CO)_xP(OPh)_y$ that are stable and active in THF as a solvent.

In the hydroformylation of 1-octene, the rhodium catalyst (XLII) modified with bulky diphosphite ligand (XXII) gives very high rate and selectivities. The

regioselectivity is caused by the steric repulsion of the diphosphite that coordinate bisequatorially to the rhodium center. The same catalyst showed very low activity and selectivity for the internal alkenes.

CHAPTER 3

3.0 SOLUBLE RHODIUM CATALYZED BIPHASIC HYDROFORMYLATION OF ALKENES

3.1 Introduction

The hydroformylation of olefins is one of the most important industrial processes that use transition metals as catalysts. Rhodium complexes are the most efficient catalysts for this reaction in terms of both catalytic activity and selectivity (6,7). When the continuous distillation of the aldehydes from the reaction mixture is not feasible, different strategies have been attempted to overcome the problem of the recovery of the precious metals from the reaction mixture. Molecular catalysts immobilized on different types of supports have been widely explored; nevertheless, the low catalytic activity and the leaching out of these supported catalysts remain a challenge in this area (102).

The aqueous biphasic hydroformylation of propene to butanal by Ruhrchemie / Rhone-Poulenc process was applied successfully at industrial scale. Water-soluble rhodium catalyst can be easily and completely separated from water insoluble products but this approach is less efficient for higher olefins. The reason is that the catalytic reaction occurs in aqueous phase; therefore, the application of aqueous biphasic system is limited by the solubility of the olefins in the water phase (26). Many approaches have been proposed to overcome the mass transport limitations that are typical in the conventional aqueous biphasic system. Among these approaches, a fluorous biphasic hydroformylation was developed by Horvath and Rabai (103). The method is based on the

limited miscibility of fluorinated solvent and fluorinated ligand in hydrocarbon. However, it is questionable whether the flourous biphasic will achieve any breakthrough in the large-scale industry, because of the toxicity of perfluorous solvents and ligands and risks related to ozone depletion (38,46).

3.1.1 Thermomorphic biphasic hydroformylation

The concept of thermomorphic biphasic catalysis involves the use of a system that itself reversibly changes from biphasic to monophasic as a function of temperature (40-49). Fully thermomorphic behavior has been noted in flourous biphasic hydroformylation developed by Horvath and Rabai (103), using fluorinated ligand and perfluorinated methylcyclohexane / n-heptane solvent system. Similarly Bianchini et al. carried out biphasic hydroformylation using $[Rh(COD)(sulphos)]^+$ as rhodium precursor, in aqueous methanol / isooctane solvent system (47).

Thermomorphic biphasic system was used in tandem isomerization-hydroformylation of *trans*-4-octene to n-nonanal using $[Rh(acac)(CO)_2]$ and BIPHEPHOS ligand, in both monophasic propylene carbonate (PC) (104) and PC/docecane/xylene multicomponent solvents system (50). And most recently, the thermomorphic biphasic system was used in the hydroaminomethylation of 1-octene using PC/dodecane/ morpholine solvent system (105).

This chapter includes the use of an inexpensive, simple, and conventional ligand such as $P(OPh)_3$ to develop a thermomorphic biphasic rhodium system to catalyze the hydroformylation of higher olefins ($> C_6$). The catalyst system enhances both catalytic activity and selectivity and also improves the recycling of the reaction of the hydroformylation of alkenes and subsequently minimizing the catalyst deactivation and

loss. The effects of various reaction parameters on the thermomorphic biphasic catalytic system were carefully studied (section 3.3.1-3.3.9).

3.1.2 Thermoregulated phase transfer biphasic hydroformylation

It is well known that the water-solubility of nonionic surfactants with polyoxyethylene moieties as the hydrophilic group is based on the hydrogen bonds formed between polyether chains and water molecules (106). The solubility of this type of surfactant decreases with a rise in temperature, and their aqueous solutions will undergo an interesting phase separation process (a miscibility gap) on heating to the ‘‘cloud point’’. A reasonable explanation attributes this phenomenon to the cleavage of hydrogen bonds. In addition, it is worth mentioning that such a process is a reversible one since the water-solubility could be restored on cooling to a temperature lower than the cloud point (107). Based on the cloud point of phosphines modified with polyoxyethylene chains, TRPTC has been proposed. The general principle of TRPTC is depicted in Figure 1.2.

The introduction of TRPTC is free from the shortcomings of classical biphasic catalysis, in which the scope of application is restrained by the water-solubility of the substrate. Moreover, the thermoregulated phase-transfer catalyst can be separated and recycled by simple phase separation. Additionally, based on the critical solution temperature (CST) of nonionic surface-active phosphine ligands in certain organic solvents, a novel biphasic catalytic system named thermoregulated phase-separable catalysis (TPSC) has been proposed (35). The basic property of the catalytic system is the monophasic reaction combined with the biphasic separation. The general principle of TPSC is depicted in Figure 1.3.

The concepts of TRPTC and TPSC have already been successfully applied in the hydroformylation and hydrogenation of higher olefins. In addition, the CO selective reduction of nitroarenes has also been realized using the TRPTC process. Thermoregulated ligands (TRL) (108) are generally defined as a kind of nonionic surface-active phosphine ligands containing polyoxy-ethylene chains as the hydrophilic group in the molecular structure, which demonstrates a special property of inverse temperature-dependent solubility in water (cloud point). Several papers involving the synthesis of polyether bound phosphines have been published. Okano et al prepared tertiary phosphines by Grignard reactants (109), and Harris et al. synthesized high molecular weight phosphines through the functionalization of poly(ethylene glycols) (110). Though not claimed by the authors, these ligands could hardly have an inverse temperature-dependent solubility in water, since these compounds have no suitable hydrophile–lipophile balance (HLB). Bergbreiter et al. previously reported a catalytic system based on nonionic water-soluble phosphine–rhodium compounds, which exhibits a special property of inverse temperature dependent solubility (29). Jin and co-workers synthesized a series of nonionic surface-active water-soluble phosphines (TRL) by introducing polyoxyethylene moieties to phosphines (111).

This chapter include the results of using $RhCl_3.3H_2O$ / N,N-dipolyoxyethylene-substituted-2-(diphenylphosphino) phenyl amine (DPPPA-PEO) / H_2O / toluene and $[Rh(CO)(\mu\text{-imidazole})(DPPPA\text{-}PEO)]_2$ / DPPPA-PEO / H_2O / n-heptane catalytic systems in thermoregulated phase transfer hydroformylation (section 3.4.1 and 3.4.2) and $Rh(CO)_2(acac)$ / DPPPA-PEO / n-heptane and $Rh(CO)_2(acac)$ / binaphtyl phosphite-PEO / n-heptane catalytic systems in thermoregulated phase separable hydroformylation (section 3.4.3).

3.2 Experimental Section

3.2.1 General

$HRhCO(PPh_3)_3$ and other rhodium complexes were purchased from Strem Company. Alkenes were purified by passing through neutral alumina, propylene carbonate was purchased from BDH chemicals and used without purification, and all other solvents were purchased from Sigma–Aldrich and were purified prior to usage.

^1H and ^{13}C NMR spectra were recorded on 500 MHz Joel 150 NMR machine. Chemical shifts were reported in ppm relative to tetramethyl silane (TMS) using $CDCl_3$. Gas chromatography analyses were realized on HP-6890-plus GC equipped with 30 m capillary column (HP-1) and FID detector.

3.2.2 General procedure for thermomorphic biphasic hydroformylation of alkenes

A typical experimental procedure is as follow: 5.0 mmol of 1-octene, 0.005 mmol of $HRhCO(PPh_3)_3$ and 0.060 mmol of $P(OPh)_3$ were dissolved in a mixture of 2.0 ml of propylene carbonate and 4.0 ml of n-heptane and placed in the glass liner of a 45 ml Parr autoclave. The autoclave was purged three times with carbon monoxide, pressurized with 200 psi of $CO + H_2$ and then heated in an oil bath with temperature controller fixed at 90 ^oC. After 1.5 h the reaction mixture was cooled to room temperature and the biphasic reaction mixtures were separated. Aldehydes, present mainly in n-heptane phase, were identified by GC and GC-MS using n-decane as an internal standard. The ^1H and ^{13}C NMR of the products gave excellent spectral data compared to authentic samples.

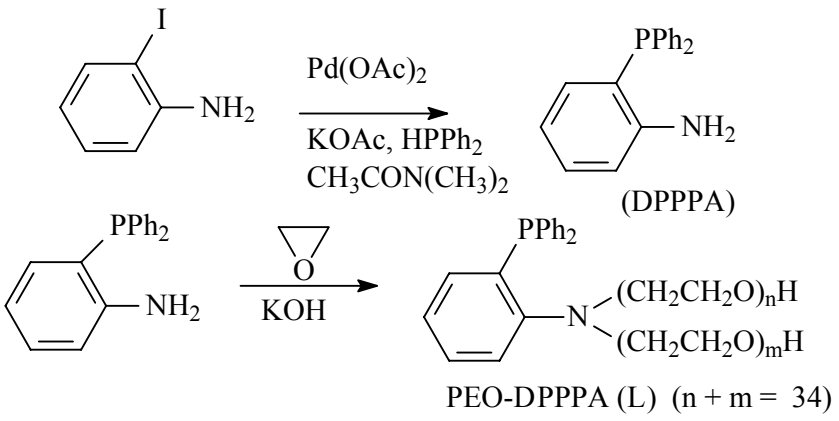
3.2.3 General procedure for thermoregulated phase transfer biphasic hydroformylation of alkenes

A typical experimental procedure is as follow: 5.0 mmol of 1-octene, 0.005 mmol of $RhCl_3.3H_2O$ or $[Rh(\mu\text{-imd})(CO)(DPPPA\text{-}PEO)]_2$ and 0.010 mmol of DPPPA-PEO were dissolved in a mixture of 4.0 ml of water and 4.0 ml of n-heptane and placed in the glass liner of a 45 ml Parr autoclave. The autoclave was purged three times with carbon monoxide, pressurized with 600 psi of CO + H_2 and then heated in an oil bath with temperature controller fixed at 120 ^oC. After 16 h the reaction mixture was cooled to room temperature and the biphasic reaction mixtures were separated. The organic phase was dried with anhydrous $MgSO_4$. Products were identified by GC and GC-MS using n-decane as an internal standard. The ^1H and ^{13}C NMR of the products gave excellent spectral data compared to authentic samples.

3.2.4 Preparation of N,N-dipolyethylene-substituted-2-(diphenylphosphino) phenylamine (DPPPA-PEO)

In a clean and dry three necked round-bottomed flask were placed 2.83 g of (0.01 mol) 2-I-$C_6H_4NH_2$, 1.19 g (0.012 mol) of KOAc, 2.24mg of $Pd(OAc)_2$ and 10.0 ml of $CH_3CON(CH_3)_3$. The system was flushed 3 times with nitrogen and heated in an oil bath to 130 ^oC. When the temperature reached 130 ^oC, 1.8 g of Ph_2PH (0.01mol) was added to the system. The reaction was kept at that temperature for 15 h, and then cooled. The materials in the flask were poured in 20.0 ml distilled water and extracted 3 times with a total of 25.0 ml of CH_2Cl_2. The extracts were combined, dried and distilled. The resulting brown solid on recrystallization from 95 % ethanol yielded 24.5 g (72 %) yield of a colorless product.

The ethoxylation of DPPPA was carried out in a 45 ml autoclave equipped with a magnetic stirrer. 1.0 g (3.6 mmol) of DPPPA and 3.0 ml of anhydrous ethanol were added into the autoclave. The system was purged with nitrogen and heated to 100 ^{o}C. Then the desired amount of ethylene oxide was added to maintain a pressure of 0.4 Mpa for 8 h. After ethoxylation, the solvent was removed in vacuum and PEO-DPPPA (n = 3) left in the autoclave. Then 20 mg of KOH and 3 ml of toluene were added. The autoclave was purged with N_2 and heated to 100 ^{o}C; ethylene oxide was added to maintain a pressure of 0.4 MPa. After the desired amount of ethylene oxide was added, the reaction was continued for 30 min (33). Toluene was then removed giving a yellowish waxy solid product. The average length was determined by ^{1}H NMR spectroscopy (16). analytical data are for DPPPA-PEO (n + m = 34) are: ^{1}H NMR (δ, ppm): 6.8-7.9 (m, Ar-H), 3.5-3.8 (br, s, -CH_2O-, -OH); ^{13}C NMR (δ, ppm): 133.4, 132.5, 131.3, 128.1, 127.6, 78.9, 75.8, 72.1, 70.0, 60.1, 42.3; ^{31}P NMR (δ, ppm): 39.8, FT-IR (KBr: ν, cm^{-1}) 3422, 2883, 1588, 1467, 1280, 1116, 843 (Appendix Figure A3.1).



Scheme 3.1

3.2.5 Preparation of [Rh(CO)(μ-imid)(DPPPA-PEO)]$_2$ (LI)

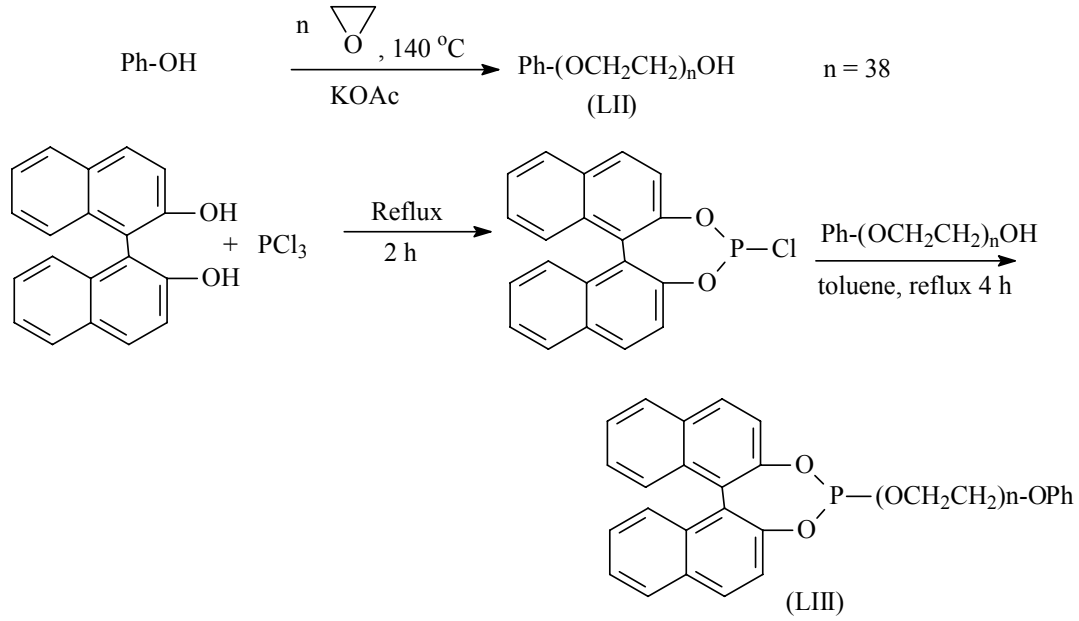
The [Rh(CO)(μ-imid)]$_2$ complex was prepared as reported in (112). [Rh(CO)(μ-imid)(DPPPA-PEO)]$_2$ was prepared as follows: a solution of 0.2 mmol of DPPPA-PEO methanol (10 ml) was added to the solution of [Rh(CO)(μ-imid)]$_2$ (0.1 mmol) in 20 ml of methanol under nitrogen atmosphere. After stirring for 20 minutes, the solution was concentrated; a yellow solid was obtained after addition of diethyl ether. Analytical data for [Rh(CO)(μ-imid)(DPPPA-PEO)]$_2$ are: ^{1}H NMR (δ, ppm): 5.8-7.9 (m, Ar-H), 3.5-3.8 (br, s, -CH_2O-, -OH); ^{31}P NMR (δ, ppm): 33.3 (Appendix Figure A3.2.)

3.2.6 Preparation of binaphthyl phosphite polyethylene oxide

The ethoxylation of phenol was carried out in a 45 ml autoclave equipped with a magnetic stirrer. 1.0 g of phenol and 20 mg of potassium acetate and 3 ml of toluene were added. The autoclave was purged with N_2 and heated to 140 ^oC; ethylene oxide was added to maintain a pressure of 0.4 MPa. After the desired amount of ethylene oxide was added, the reaction was continued for 30 min. Toluene was then removed giving a yellowish waxy solid product. The average length was determined by ^{1}H NMR spectroscopy (Ph-$(OCH_2CH_2)_n$-OH) (22) (Appendix Figure A3.3).

6.5 ml of PCl_3 was added to a 100-ml, round bottom flask which contained 5.5 g of binaphthol over a 30 minutes period. After the addition, the mixture was stirred at refluxing for 2 h. Distillation afforded 80 % of binaphthyl chlorophosphite. 0.004 mol of the binaphthyl chlorophosphite in 5.0 ml toluene was added to a stirred solution of Ph-$(OCH_2CH_2)_n$-OH (0.002mol) in 10 ml of toluene. After the addition, the mixture was refluxed for 4 h under nitrogen. Toluene was drawn under vacuum. The crude product was dissolved in ether for further purification (22). Analytical data are for binaphtyl

phosphite polyethylene oxide (n = 38) are: ^{1}H NMR (δ, ppm): 8.0-7.0 (m, arom.-H), 4.1-3.4 (br, s, -CH_2O-); ^{13}C NMR (δ, ppm): 152.5, 133.5, 130.0, 129.7, 128.6, 127.9, 127.6, 126.4, 126.2, 125.8, 124.6, 124.2, 122.8, 121.3, 118.1, 72.3, 71.4, 70.0, 67.8, 65.3; ^{31}P NMR (δ, ppm): , FT-IR (KBr: ν, cm^{-1}) 3449, 3050, 2870, 1619, 1589, 1507, 1464, 1384, 1213, 1083, 818 749, 695 (Appendix Figure A3.4).

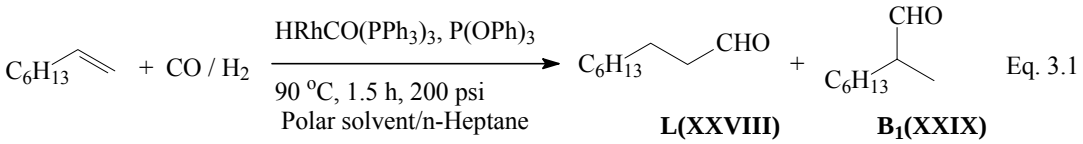


Scheme 3.2

3.3 Results and discussion

3.3.1 Thermomorphic biphasic hydroformylation*:* Effect of the type of polar solvents

Hydroformylation of 1-octene, chosen as a model substrate, into nonanal (**L_1** or n) and 2-methyl octanal (**B_1** or i) occurred smoothly at relatively mild conditions [90 °C, 200 psi (CO / H_2= 1:1), 90 minutes], with $HRhCO(PPh_3)_3$ used as catalyst and $P(OPh)_3$ used as a ligand in polar / non-polar biphasic (thermomorphic) solvent system (Eq. 3.1).

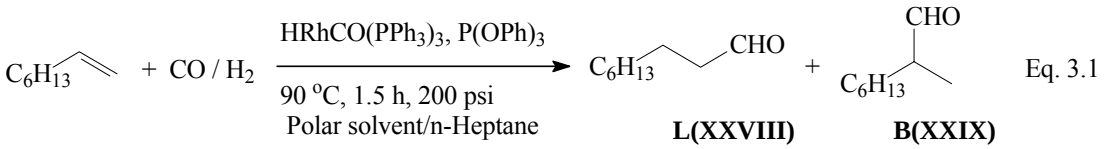


L(XXVIII) **B_1(XXIX)** Eq. 3.1

The most suitable biphasic solvent system which led to high selectivity towards the desired linear products included propylene carbonate and n-heptane. The total yield of aldehydes reached 84 % with n / i ratio of 8.1 (88 / 11) and 10 (90 / 10) in n-heptane and propylene carbonate phases, respectively (Table 3.1, entry 6). The system that used DMSO / n-heptane mixture showed almost the same selectivity in linear aldehyde but a lower total yield (70 %). Propylene carbonate was previously described as a good solvent with rhodium precursor [Rh(acac)$(CO)_2$] and BIPHEPHOS ligand (50). Dimethylformamide (DMF) was always considered as an important solvent for practical purposes and was used largely as an aprotic protophilic medium in many organic and inorganic reactions (113). In addition, DMF / n-heptane biphasic system gave in the hydroformylation of 1-octene, a combined yield of 80 % of aldehydes with n / i ratio of 82 / 18 in n-heptane and 87 / 13 in DMF phase. The disadvantage of using DMF was that the aldehydes as products have more affinity towards DMF phase (yield = 45 %) compared to n-heptane phase (yield = 35 %) (Table 3.1, entry 1).

Another system formed of DMA (N,N-dimethylacetamide) and n-heptane, which were immiscible at room temperature and miscible at any temperature above 65 ^{o}C (114), was used in the hydroformylation of 1-octene. The total yield of aldehydes was very high (83 %), but a non-separable mixture of solvents was obtained at the end of the hydroformylation reaction (Table 3.1, entry 4). Interestingly, formamide / n-heptane biphasic system gave the highest distribution coefficient of the products between the n-heptane phase (69 %) and the formamide phase (5 %) (Table 3.1, entry 7), but

Table 3.1. Thermomorphic Biphasic Hydroformylation of 1-octene: Effect of the type of Polar Solvent.[a]



L(XXVIII) **B(XXIX)** Eq. 3.1

Entry	Solvent Mixture	n-Heptane		Polar Solvent	
		Yield[b] %	B / L[c]	Yield[b] %	B / L[c]
1	DMF / n- Heptane	45	18 / 82	35	17 / 83
2	DMSO / n- Heptane	62	11 / 89	8	10 / 90
3	CH_3CN / n- Heptane	52	12 / 88	25	11 / 89
4[d]	DMA / n- Heptane	-	-	83	21 / 79
5	N-Methylformamide / n-Heptane	50	22 / 78	27	17 / 83
6	PC / n-Heptane	65	11 / 89	12	10 / 90
7	Formamide / n-Heptane	69	16 / 84	5	16 / 84
8[e]	Nitromethane / n-Heptane	50	15 / 85	18	14 / 86

a) Reaction conditions $RhHCO(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), polar solvent (2.0 ml), n-heptane (4.0 ml), 90 °C, 1.5 h, 1-octene (5.0 mmol), 100/100 psi CO / H_2,
b) Determined by GC using 1-decane as internal standard.
c) Determined by GC and ^1H NMR
d) No phase separation.
e) 16 h.

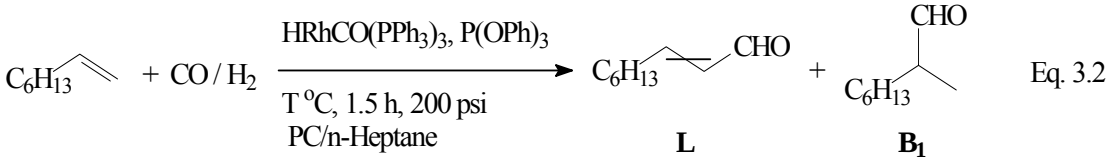
unfortunately a significant amount of rhodium catalyst moved to the n-heptane phase, which is supposed to contain the majority of the aldehyde products, and subsequently the rhodium catalyst could not be recycled.

The system formed of nitromethane and n-heptane, which has shown high efficiency in Sonogashira and Suzuki coupling reaction of aryl bromide with alkynes, gave no products after 1.5 h (46). However, after 16 h of reaction, a combined yield of 68 % was obtained with n / i ratio of 5.7 (85 / 15) and 6.1 (86 / 14) in n-heptane and nitromethane, respectively (Table 3.1 entry 8). The analysis of the results obtained with the above-mentioned different biphasic solvent systems helped us to select the thermomorphic system that includes propylene carbonate and n-heptane as the most suitable system that will be considered in our further studies.

3.3.2 Thermomorphic biphasic hydroformylation*:* Effect of the Rhodium complexes and ligands

In addition to the effects of the type of polar solvents, the effect of the type of the rhodium catalyst in the reaction of hydroformylation of 1-octene was also studied in the presence of triphenylphosphite, $P(OPh)_3$. $RhCl_3.3H_2O$ showed a little catalytic activity in the conversion of 1-octene into aldehydes even after 16 h of reaction. While $[RhCl(COD)]_2$ and $Rh_6(CO)_{16}$ gave good total yields of aldehydes (70 and 66%, respectively) and moderate to good selectivities in linear aldehydes (Table 3.2, entries 2-3). The results obtained showed that $Rh(CO)_2(acac)$ or $HRh(CO)(PPh_3)_3$ combined with $P(OPh)_3$ represents the most suitable catalytic system for the hydroformylation of 1-octene in the thermomorphic biphasic solvent mixture formed of propylene carbonate and n-heptane.

Table 3.2. Thermomorphic biphasic hydroformylation of 1-octene: Effect of rhodium complexes.[a]



Eq. 3.2

Entry	Rh (mmol)	n-heptane phase			Propylene Carbonate phase		
		Yield[b] %	B/L % ratio[c]	n/i ratio	Yield[b] %	B/L % ratio[c]	n/i ratio
1	$Rh(CO)_2(acac)$ (0.005 mmol)	67	17/83	4.9	11	15/85	5.7
2	$[RhCl(COD)]_2$ (0.025 mmol)	60	18/82	4.6	10	16/84	5.3
3	$Rh_6(CO)_{16}$ (0.001mmol)	57	24/76	3.2	9	22/78	3.6
4	$HRh(CO)(PPh_3)_3$ (0.005 mmol)	65	11/89	8.1	12	10/90	10
5[d]	$RhCl_3.3H_2O$ (0.005 mmol)	6	32/68	2.1	2	28/72	2.6
6[b]	$HRh(CO)(PPh_3)_3$ (0.005 mmol)	10	17/83	4.9	2	15/85	5.7
7[c]	$HRh(CO)(PPh_3)_3$ (0.005 mmol)	42	15/85	5.7	7	13/87	6.7

a) Reaction conditions: $P(OPh)_3$ (0.06 mmol), Propylene carbonate (2.0 ml), n-heptane (4.0 ml), 1-octene (5.0 mmol), 90 °C, 1.5h, 100/100 psi CO/H_2,
b) Determined by GC using 1-decane as internal standard.
a) Determined by GC and ^1H NMR.
b) 16 h.
c) 0.06 mmol $P(OEt)_3$, 6 h.
d) 0.06 mmol PPh_3.

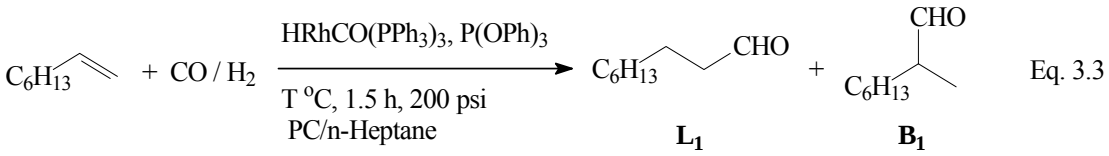
Also, the effect of the addition of different monophosphine and monophosphite ligands such as PPh_3, $P(OEt)_3$ and $P(OPh)_3$, was studied. It was observed that $P(OPh)_3$ was the most efficient ligand where the hydroformylation of 1-octene led to a moderate yield (65 %) and an excellent ratio of n / i (8.1) in n-heptane phase after 1.5 h. However, PPh_3 gave a total yield of 42 % and a ratio of n / i of 5.7 under the same conditions. The lowest yield (10 %) of the products was obtained with $P(OEt)_3$ as a ligand in n-heptane after 6 h of reaction.

3.3.3 Thermomorphic biphasic hydroformylation*:* Effect of the temperature

The change of the temperature has a major effect on the distribution of the products due to the involvement in the hydroformylation / isomerization of the double bonds and the dissociation of ligand from the catalytic complexes at higher temperature (2). A systematic study on the influence of the temperature on the regioselectivity and the catalytic activity in the hydroformylation of 1-octene in the biphasic system of propylene carbonate and n-heptane was carried out at a variety of temperatures ranged from 70 ^{o}C to 140 ^{o}C. The results are shown in Figure 3.1. The formation of the linear aldehydes prevailed in all cases at all temperatures. With the increase of the temperature, however, an increase of the amount of the linear aldehydes was observed up to 90 ^{o}C above which the percentage in linear aldehydes started dropping.

At 70 ^{o}C, the isolated yield of aldehydes in n-heptane phase was very low (8 %). An increase of the temperature by 10 ^{o}C resulted in doubling (20 %) the yield of aldehydes. The yield of the products in n-heptane phase reached its maximum at 120 ^{o}C (68 %) then dropped to 54 % at 130 ^{o}C. The ratio of n / i aldehydes increased from 4.3 at

Thermomorphic biphasic hydroformylation of 1-octene: Effect of the Temperature



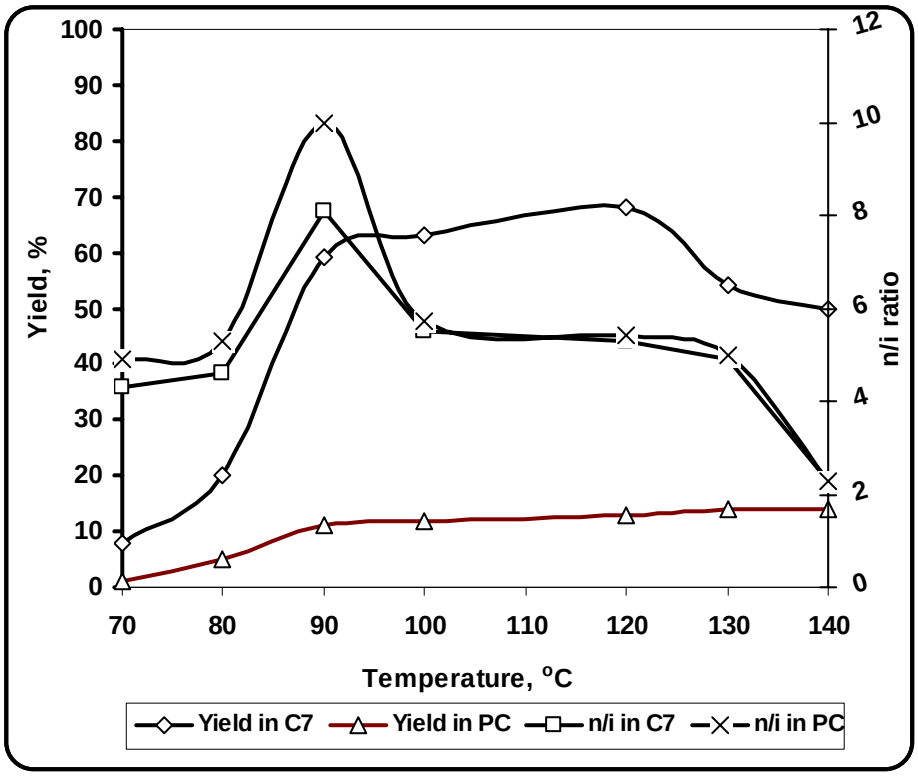


Figure 3.1. Hydroformylation of 1-octene by $HRh(CO)(PPh_3)_3$. Effect of the temperature. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), Propylene carbonate (2.0 ml), n-heptane (4.0 ml), 1-octene (5.0 mmol), CO/H_2 200 psi 1:1, 5 h.

70 ^{o}C to 8.1 at 90 ^{o}C then dropped to 5.3 at 100 ^{o}C and finally to 2.1 at 140 ^{o}C in n-heptane phase. Similar trends were observed in PC phase, with slightly higher n / i ratio in all cases. There are two possible reasons that may explain this observation at high temperature: the first is related to an increase in the isomerization of 1-octene into other internal octenes and subsequently increased the amount of the branched isomers, hence lower n / i ratio. The second reason is due probably to the dissociation of the ligand from the rhodium complex leading to a lower linear product. These two reasons also account for the decrease in the total yields of aldehydes at higher temperature.

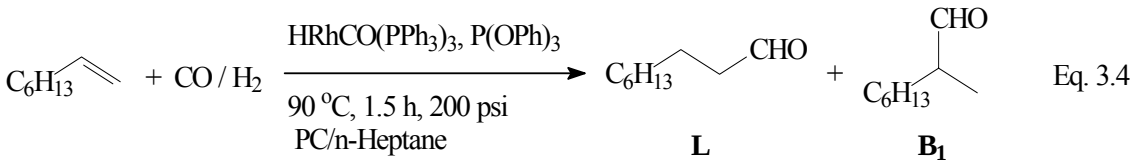
Similar observation was made in the hydroformylation of 1-hexene where at T < 80 ^{o}C a slight increase in linear isomer occurred, whereas at T >100 ^{o}C the opposite is true, probably because of the increase of double-bond isomerization (115).

3.3.4 Thermomorphic biphasic hydroformylation*:* Effect of total pressure (CO:H_2 = 1:1)

In carbonylation reaction, a minimum pressure of CO and hydrogen is needed to dissolve sufficient amount of these gases in the reaction medium (2). Figure 3.2 summarizes the effect of the total pressure (CO: H_2 = 1:1) on the yield and the selectivity of the reaction. Generally, an increase in the total pressure increases the total yield of the aldehydes but decreases the percentage of the linear isomer.

Only 16 % total yield in both phases was obtained when a total pressure of 50 psi (25 / 25 psi of CO / H_2) was used, the total yield increased to maximum of 90 % for the total pressure of 400 psi, then decreased to 88 % for total pressure of 600 psi. The rate vs. CO concentration passes through maximum indicating negative-order

Thermomorphic biphasic hydroformylation of 1-octene: Effect of the CO / H_2 total pressure



Eq. 3.4

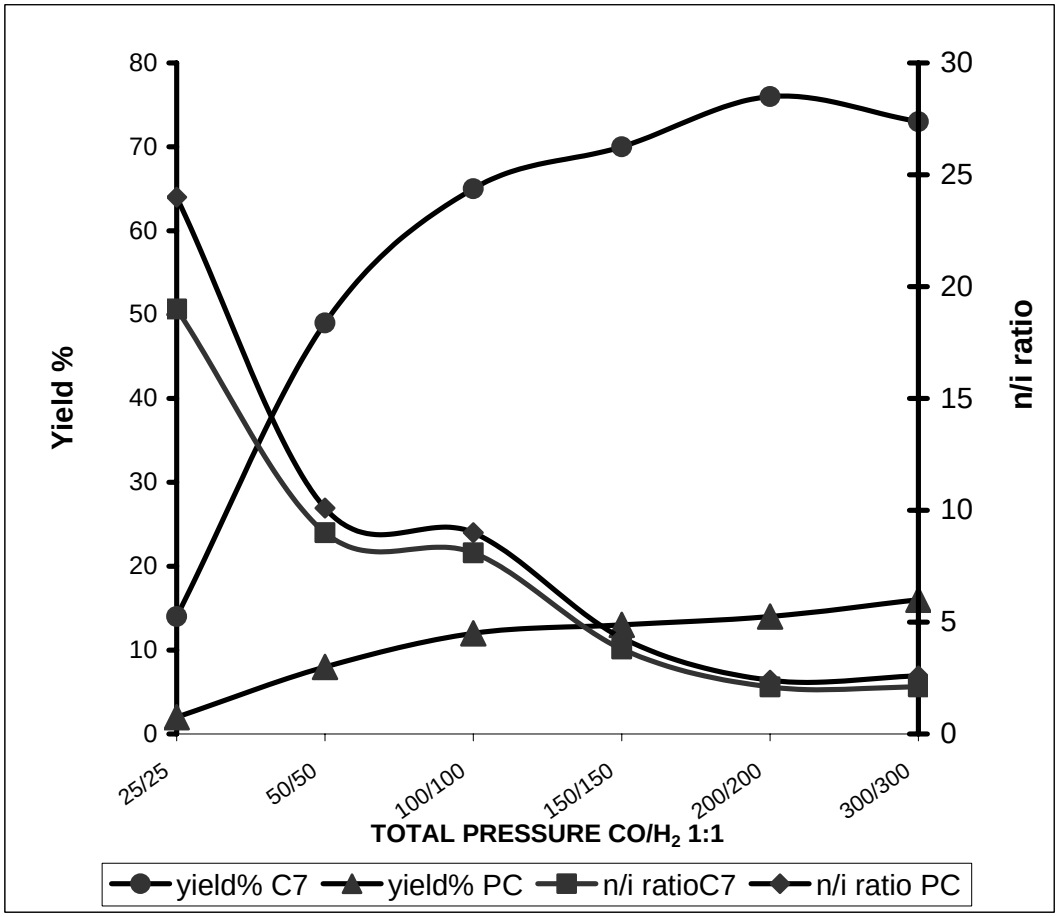
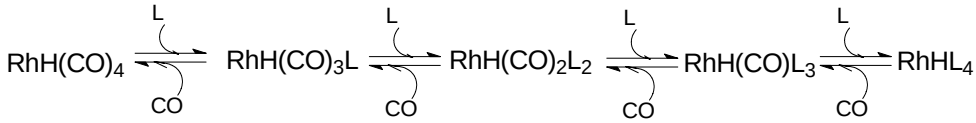


Figure 3.2. Hydroformylation of 1-octene by $HRh(CO)(PPh_3)_3$. Effect of the CO / H_2 total pressure (1:1). Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), Propylene carbonate (2.0 ml), n-heptane (4.0 ml), 1-octene (5.0 mmol), 90 °C, 1.5 h.

dependence at higher pressure (115). However, n / i ratio in n-heptane phase decreased from 19 at 50 psi to 8.1 at 200 psi and finally to 2.1 at 400 and 600 psi. Similar trend with slightly higher n/i ratios were observed in propylene carbonate phase. These results could be rationalized based on the change in equilibria among the active species (equation 3.5). High CO pressure shifts the equilibrium to left to form the more active but less selective species (116).

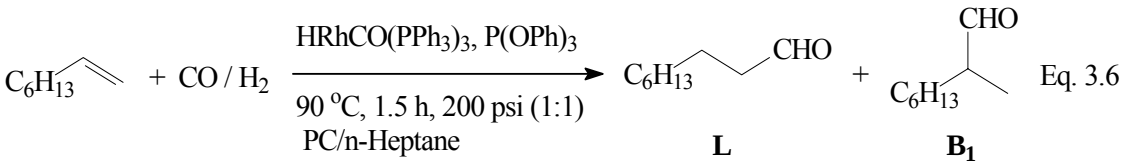


Eq. 3.5

3.3.5 Thermomorphic biphasic hydroformylation*:* Effect of partial pressures CO:H_2

The ratio of the partial pressure of CO and H_2 affects both the rate and the composition of the isomers. The effect of CO / H_2 ratio at total pressure of 400 psi was studied with the catalytic system $HRhCO(PPh_3)_3$-$P(OPh)_3$-PC/n-heptane biphasic system. The results shown in figure 3.3, indicate an increase in the total yield in the two phases from 77 % in 50 / 350 CO / H_2 (1/7) to 92 % in 1/3, then decreases to 90 % for 1/1, and further decreased to 65 % when 7/1 ratio CO / H_2 was used. On the other hand, a decrease in the percentage of linear isomer was observed with the increase in the proportion of CO partial pressure. The n / i ratio of 9.0, 4.9, 2.1, 2.4 and 2.4 were obtained for 1/7, 1/3, 1/1, 3/1 and 7/1 CO / H_2 ratio, respectively. From these results it can be inferred that a high hydrogen pressure increases the rate and n / i ratio (118,119), whereas a very high CO pressure produces a very active but less selective catalyst (low n / i ratio) i.e. the equilibrium moves to the left in equation 3.5.

Thermomorphic Biphasic Hydroformylation of 1-Octene: Effect of the CO / H_2 Partial Pressures



Eq. 3.6

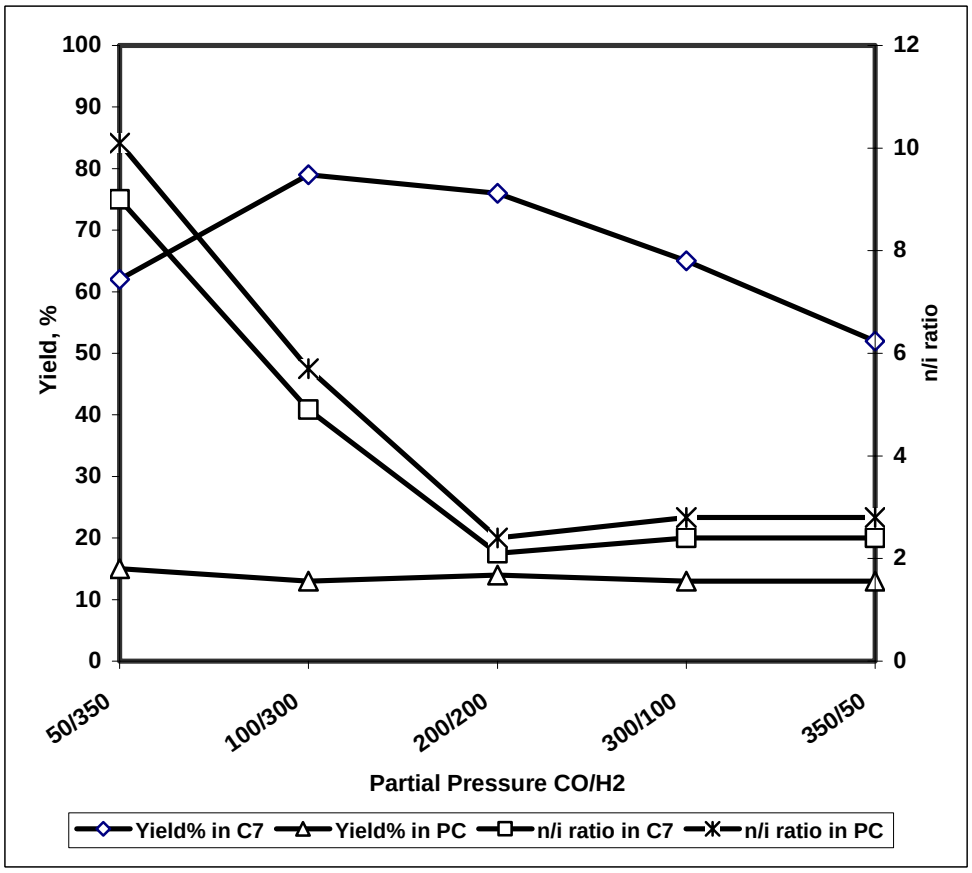


Figure 3.3 Hydroformylation of 1-octene by $HRh(CO)(PPh_3)_3$. Effect of the CO / H_2 ratio. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005mmol), $P(OPh)_3$ (0.06 mmol), Propylene carbonate (2.0 ml), n-heptane (4.0 ml), 1-octene (5.0 mmol), 400 psi CO / H_2 psi, 90 °C, 1.5 h.

3.3.6 Thermomorphic biphasic hydroformylation*:* Effect of ligand to catalyst ratio

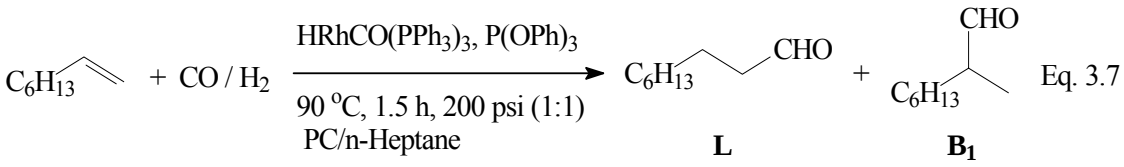
The effect of $P(OPh)_3$ / $HRh(CO)(PPh_3)_3$ molar ratios on the hydroformylation of 1-octene are shown in Figure 3.4. Very low yields (7 % in n-heptane and 2 % in propylene carbonate) were obtained in the absence of $P(OPh)_3$ due to the contribution of other side reactions such as hydrogenation and isomerization of 1-octene. Interestingly, the addition of 0.005 mmol of $P(OPh)_3$ (i.e. L / [Rh] = 1) has significantly improved the total yield of aldehydes (40% in n-heptane and 9 % in propylene carbonate). At a ratio of L / [Rh] of 12, a maximum yield (65 %) was obtained in n-heptane phase. Any further addition of $P(OPh)_3$ resulted in a decrease of the total yield due probably to the formation of stable and non-active intermediates such as $Rh_x[P(OPh_3)]_y$ in the form of dimer or trimer.

Similarly, an increase in the amount of phosphite ligand led to an increase of the n/i ratio. For example, at L / [Rh] = 1 the ratio n/i was 3.1 and it reached a maximum at about twelve fold excess of phosphite versus rhodium complex (n / i = 8.1 in n-heptane phase and 10.1 in propylene carbonate phase). A further increase in phosphite concentration caused a decrease in n / i ratio of aldehydes.

3.3.7 Thermomorphic biphasic hydroformylation of different alkenes

The hydroformylation of a variety of special alkenes occurred smoothly at relatively mild condition [90 ^oC, CO / H_2 (100/100 psi), 1.5 h] with $HRhCO(PPh_3)_3$ as a catalyst precursor and $P(OPh)_3$ as a ligand in propylene carbonate / n-heptane biphasic solvent system (Table 3.2). For example, alkyl alkenes containing tertiary carbon atom bonded to the vinyl group, such as 3,3-dimethyl-1-butene, showed excellent

Thermomorphic Biphasic Hydroformylation of 1-Octene: Effect of the ligand to catalyst ratio



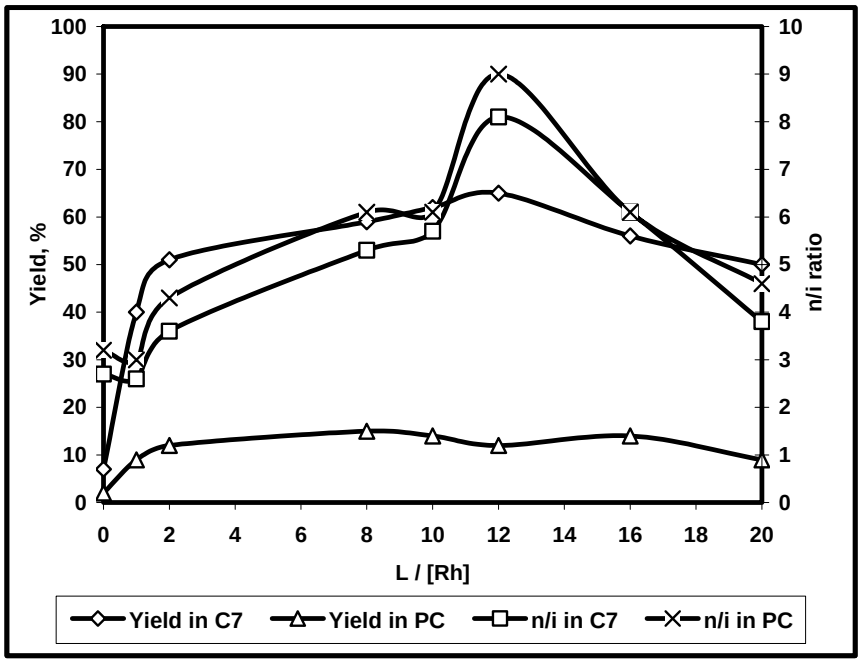
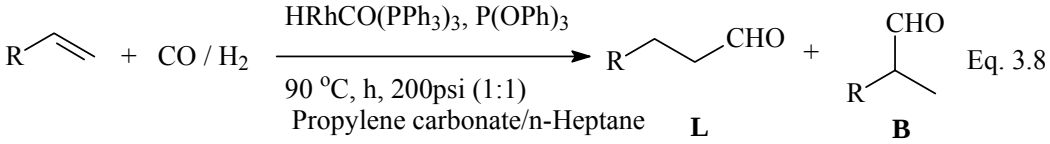
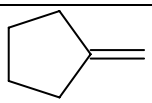
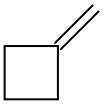
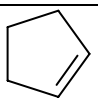
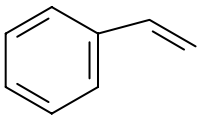


Figure 3.4. Biphasic hydroformylation of 1-octene. Effect of ligand to catalyst ratio. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), propylene carbonate (2.0 ml), n-heptane (4.0 ml), 1-octene (5.0 mmol), CO / H_2 (100/100 psi), 90 °C.

Table 3.3. **Thermomorphic Biphasic hydroformylation of different alkenes.**[a]



Eq. 3.8

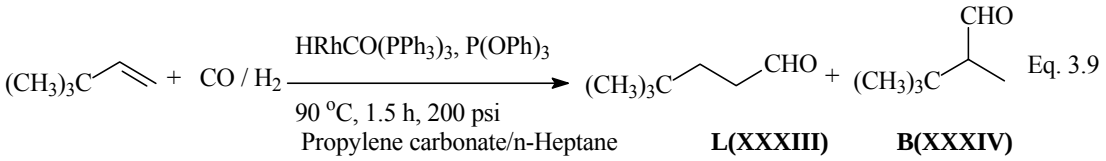
Entry	Substrates	Time h	n-Heptane		Propylene Carbonate	
			Yield[b] %	B / L[c]	Yield[b] %	B / L[c]
1	$CH_3(CH_2)_5CH=CH_2$	1.5	64	11 / 89	12	10 / 90
2	$(CH_3)_3CCH=CH_2$	1.5	22	2/98	18	2 / 98
3		1.5	28	8 / 92	31	0 / 100
4		1.5	35	3 / 97	37	0 / 100
5		2	25	0 / 100	15	0 / 100
6		1.5	20	80 / 20	60	71 / 29

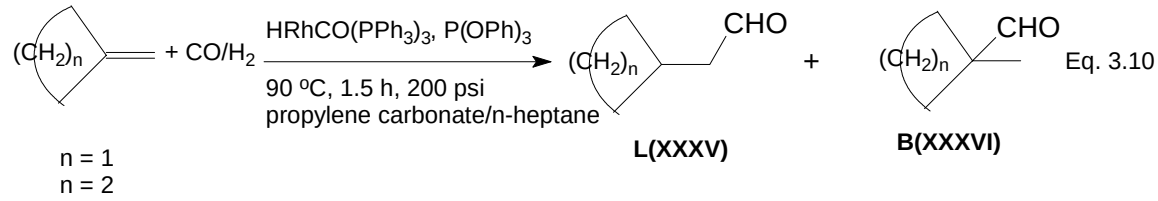
a) Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), alkene (5.0 mmol), propylene carbonate (2.0 ml), n-heptane (4.0 ml), CO / H_2 (100 / 100 psi), 90 °C.

b) Determined by GC.

c) Determined by GC and ^1H NMR.

regioselectivity where the linear aldehyde (XXXIII) was almost exclusively formed (n / i = 98 / 2 in both phases) (Eq. 3.9, Table 3.2, entry 2). The main reason for such behavior is the steric effect, which prevents the addition of CHO moiety on the internal carbon of the double bond. Similarly, methylene cylopentane was hydroformylated to give predominately the linear aldehyde 2-cylopentylethanal (XXXV) with only traces of the branched aldehyde 1,1-cyclopentyl methyl methanal (XXXVI) (Eq. 3.10, Table 3.2, entry 3). In propylene carbonate phase only XXXV (linear) was found.



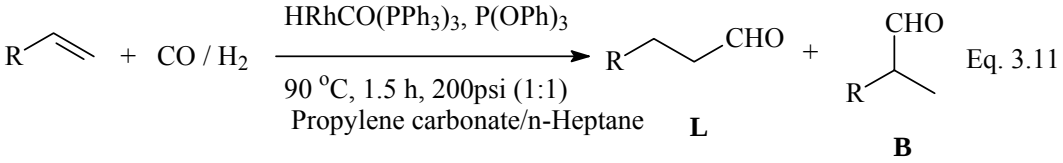


As expected, the hydroformylation of styrene occurred smoothly at the same experimental conditions in propylene carbonate / n-heptane biphasic system (Table 3.2, entry 6). The largely predominating product was the branched isomer [2-phenyl propanal, (XXIII)] in both polar phase (n / i = 18 / 82) and non-polar phase (n / i = 13 / 87). The greater yield of the aldehydes in the propylene carbonate (60 %) compared to the n-heptane phase (20 %) is due to the high polarity of the aryl aldehydes.

3.3.8 Thermomorphic biphasic hydroformylation: Effect of the chain length of alkyl alkenes

The hydroformylation of different terminal alkyl alkenes was carried out by the catalytic system $HRhCO(PPh_3)_3$-$P(OPh)_3$-CO/H_2 in the biphasic solvent composed of propylene carbonate and n-heptane (Eq. 3.10, Figure 3.5). The distribution of the aldehydes between the two phases was found to vary with the chain length. The longer is the alkyl chain length the more is the partition of its aldehydes in the favor of the product phase (n-heptane phase). This observation is related to the fact that long-chain aldehydes are less soluble in the substrate phase (propylene carbonate phase). For example, the distribution of 1-hexanal and 2-methyl pentanal, obtained from 1-pentene, between n-heptane phase and propylene carbonate phases is 62 / 38 compared to 95 / 5 in 1-pentadecanal and 2-methyl tetradecanal, obtained from 1-tetradecene.

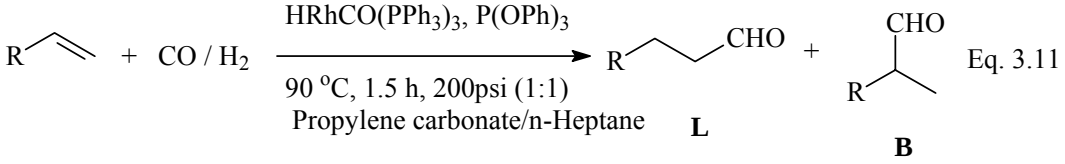
As mentioned earlier, the longer alkenes are less reactive compared to the shorter chain alkenes because of their high solubility in the catalyst phase (propylene carbonate) and also are less selective toward the linear isomer probably because of the isomerization of the double bond, which was known to increase with the chain length (2).



Eq. 3.11

R = C_3H_7, C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{15}H_{31}$

Thermomorphic Biphasic hydroformylation of different alkyl alkenes.



R = C_3H_7, C_4H_9, C_6H_{13}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{15}H_{31}$

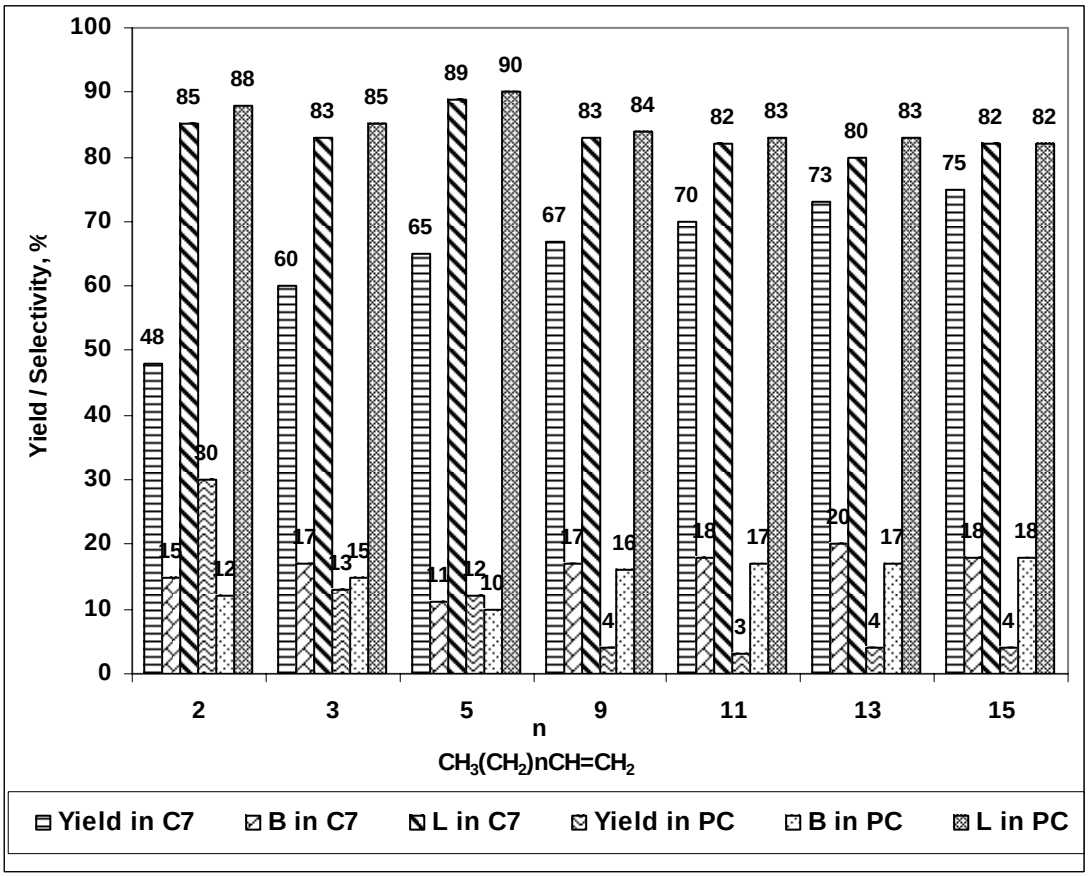


Figure 3.5. Biphasic hydroformylation of different alkyl alkenes by $HRh(CO)(PPh_3)_3$. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), propylene carbonate (2.0 ml), n-heptane (4.0 ml), alkyl alkenes (5.0 mmol), CO/H_2 (100 / 100 psi), 90 °C, 1.5 h.

3.3.9 Thermomorphic Biphasic Hydroformylation of 1-Octene: Recycling of the catalyst.

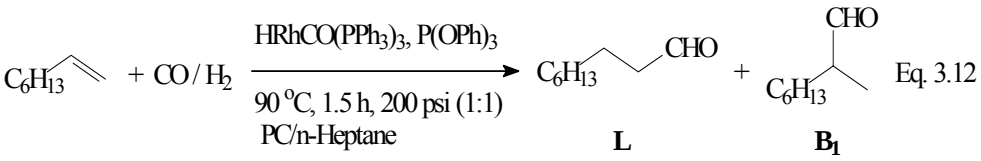
The thermomorphic biphasic hydroformylation offered advantages in product isolation and catalyst recycling. The recycling experiments were carried out under constant conditions [90 ^{o}C, 200 psi of CO / H_2 (1:1), 1.5 h, 0.005 mmol of $HRhCO(PPh_3)_3$ and 0.06 mmol of $P(OPh)_3$]. After the reaction, n-heptane phase that contained the majority of the products was separated from the reaction mixture by decantation. A fresh n-heptane and substrate was added to the propylene carbonate phase containing catalyst. The rhodium catalysts can be easily recycled by this simple technique.

Figure 3.6 contains the results of the catalyst recycling for the hydroformylation of 1-octene. A continuous decrease in the total yield and the selectivity towards the linear aldehyde was observed. The reason behind such deactivation was probably the adventitious oxidation of the triphenyl phosphite ligand to triphenyl phosphite oxide after several cycles. Traces of this oxide were detected by GC and GC-MS. Another important reason was the gradual loss of the phosphite ligand into n-heptane layer.

In order to maintain the activity and the turnover of the catalyst high, 0.015 mmol of $P(OPh)_3$ was added after each successful cycle. The results (Figure 3.7) showed that the yield was maintained excellent even after eighth cycles.

DMSO / n-heptane solvent mixture was also considered in the study of the catalysts recycling. Under the standard conditions (Figure 3.8), the yield of aldehydes and the selectivity of linear isomer were maintained after eight cycles as high as 95 % and 86 %, respectively.

Thermomorphic Biphasic hydroformylation: Recycling of the catalyst.



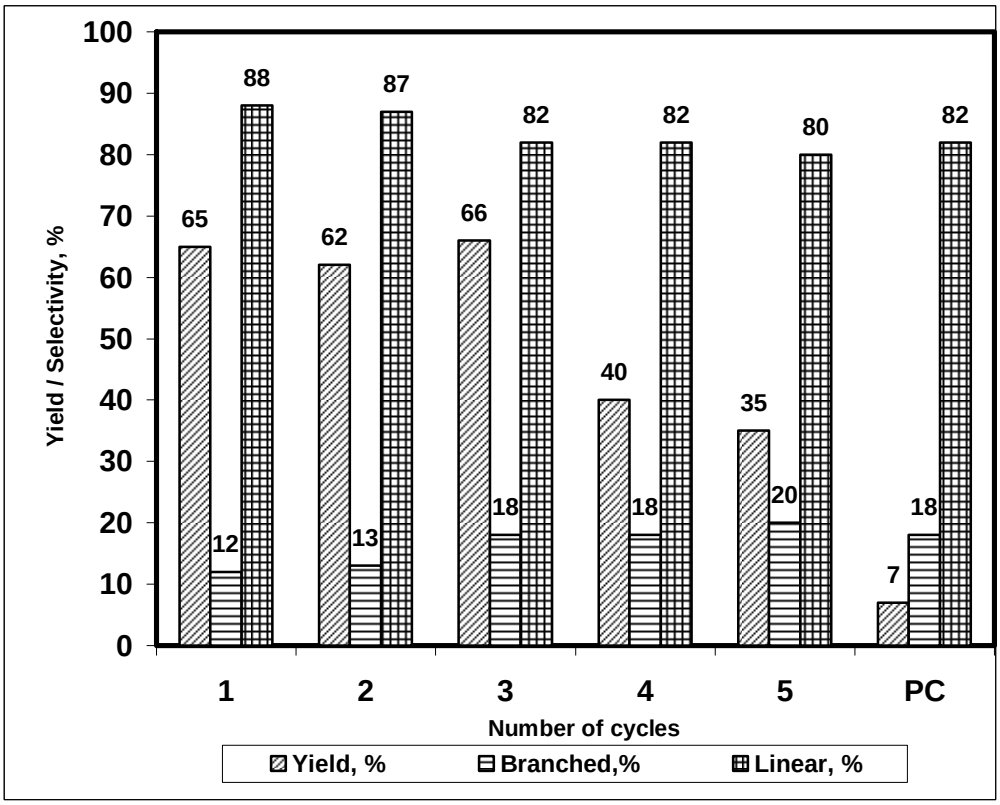
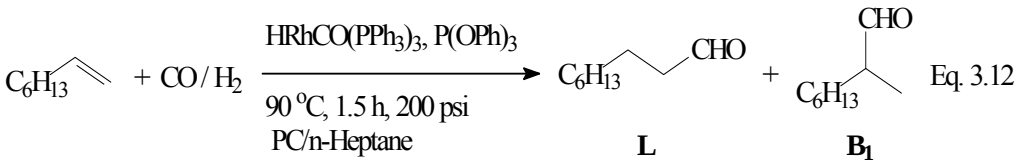


Figure 3.6. Biphasic hydroformylation of 1-octene. Recycling of the catalyst. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), **<u>no addition</u>** of $P(OPh)_3$ after each cycle, 1-octene (5.0 mmol), Propylene carbonate (2.0ml), n-heptane (4.0 ml), CO/H_2 (100/100 psi), 90 ^oC, 1.5 h.

Thermomorphic Biphasic hydroformylation: Recycling of the catalyst.



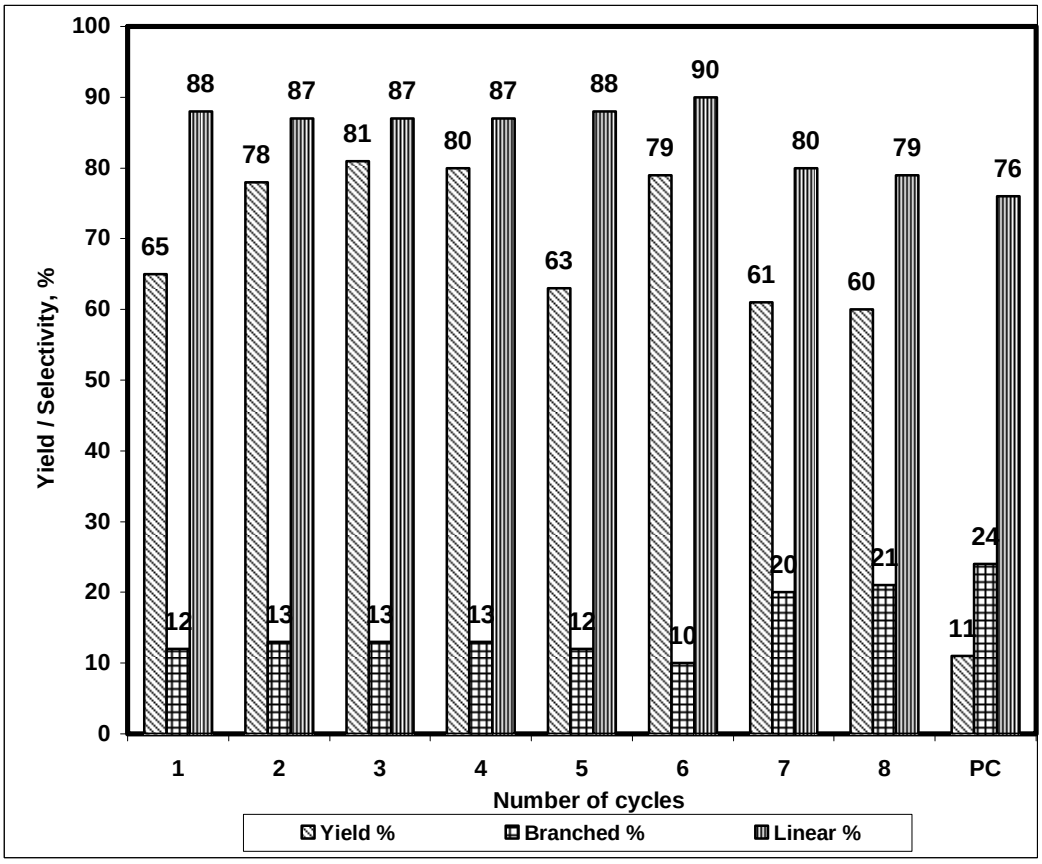
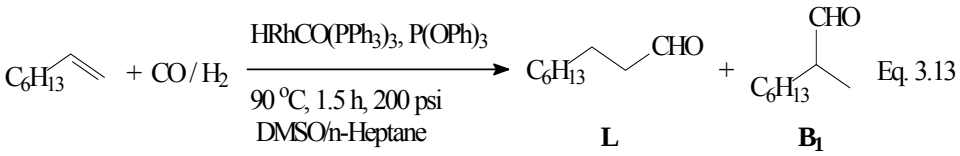


Figure 3.7.. Biphasic hydroformylation of 1-octene. Recycling of the catalyst. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), [0.015 mmol of $P(OPh)_3$ was added after each cycle], 1-octene (5.0 mmol), propylene carbonate (2.0ml), n-heptane (4.0 ml), CO / H_2 100/100 psi, 90 ^oC, 1.5 h.

Thermomorphic Biphasic hydroformylation: Recycling of the catalyst.



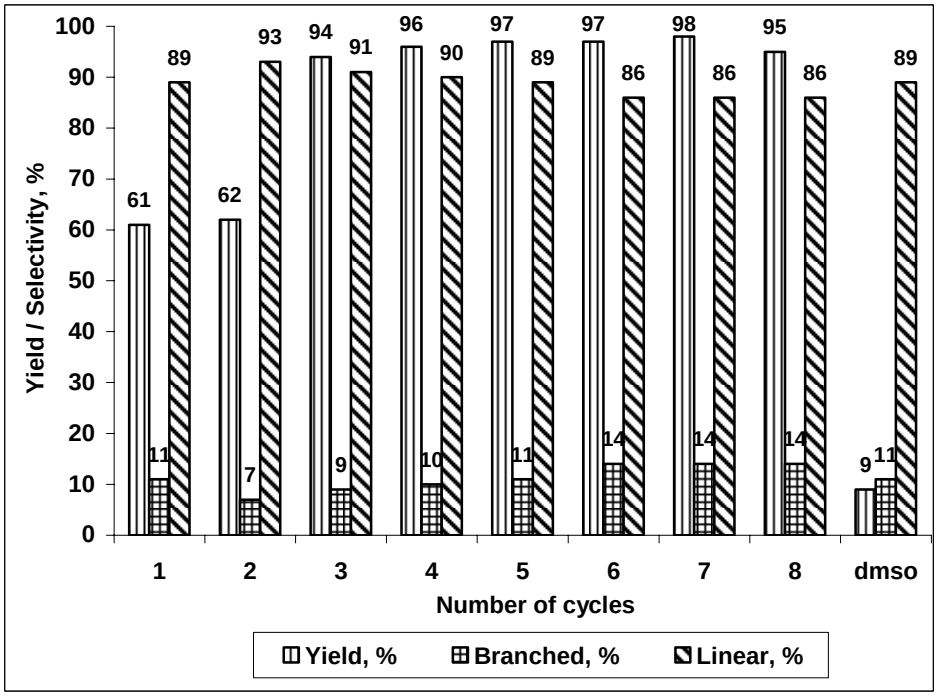


Figure 3.8. Biphasic hydroformylation of 1-octene. Recycling of the catalyst. Reaction conditions: $HRh(CO)(PPh_3)_3$ (0.005 mmol), $P(OPh)_3$ (0.06 mmol), [0.015 mmol of $P(OPh)_3$ were added after each cycle], 1-octene (5.0 mmol), DMSO (2.0 ml), n-heptane (4.0 ml), CO / H_2 (100/100 psi), 90 °C, 1.5 h.

The absence of a significant leaching out of the catalyst from the polar phase or catalyst phase is very important in order to maintain the catalytic activity and the turnover of the catalyst extremely high. However, a little loss of the catalyst during each cycle took place due to the loss of a small amount of the polar solvent (DMSO or PC) into the n-heptane layer, since a saturated n-heptane solution contains 1.1 % (vol.) of DMSO or PC (120).

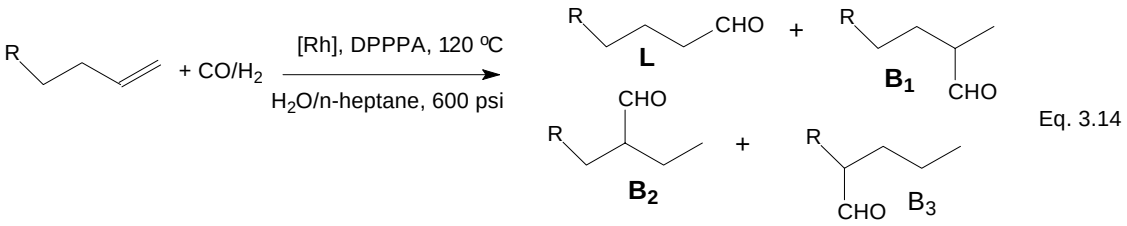
3.4 Results and discussion

3.4.1 Thermoregulated phase transfer hydroformylation

The aqueous-organic biphasic hydroformylation of 1-octene was carried out using $[Rh(CO)(\mu\text{-imidazole})(DPPPA\text{-}PEO)]_2$ as catalyst, with DPPPA-PEO as ligand, in n-heptane / H_2O solvent system. The effect of temperature on the hydroformylation of 1-octene is shown in Table 3.3 (entries 1-3). Generally, an increase in the temperature leads to an increase in the conversion of 1-octene. However, the percentage of linear aldehydes decreased as the temperature increased. The reason for this is that the isomerization of the α-olefin to internal olefin becomes faster at higher temperature. The conversion of 1-octene increased from 37 % to 63 % when the temperature raised from 80 to 100 ^oC (Table 3.3, entries 1,2); rhodium catalyst remained in the aqueous phase at lower temperature ($T < Cp$, 98 ^oC) and transferred into the organic phase at higher temperature ($T > Cp$, 98 ^oC). An optimum temperature for the reaction of 120 ^oC resulted in a conversion of 82 % and selectivity for the linear aldehydes of 45 % compared to 70 % in linear at 80 ^oC.

The effect of the ratio of CO / H_2 was studied with the catalytic system $[Rh(CO)(\mu\text{-imidazole})(DPPPA\text{-}PEO)]_2$ (Table 3.3, entries 3-5). At the total pressure of

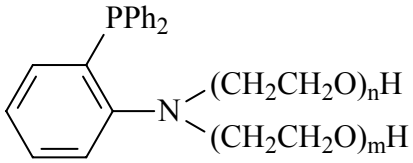
Table 3.4. Thermoregulated phase transfer hydroformylation: Effect of reaction parameters.[a]



Eq. 3.14

Entry	Substrate	CO / H_2 psi	Conv.[b] %	Product distribution[c]			
				L %	B_1 %	B_2 %	B_3 %
1[d]	1-octene	200 / 400	37	70	30	-	-
2[e]	1-octene	200 / 400	63	63	33	3	1
3	1-octene	200 / 400	82	45	36	11	8
4	1-octene	100 / 500	80	42	37	12	9
5	1-octene	400 / 200	66	51	36	8	5
6[f]	1-octene	200 / 400	6	68	32	-	-
7	styrene	200 / 400	96	46	54	-	-
8[d]	styrene	200 / 400	64	28	72	-	-
9	1-hexadecene	200 / 400	74	48	37	6	9
10[g]	β-methylstyrene	200 / 400	57	16	51	33	-
11[g]	2-octene	200 / 400	77	21	47	18	14

a) Reaction conditions: $[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$ (0.005 mmol), DPPPA (0.01 mmol), alkene (5.0 mmol), H_2O (4.0 ml), n-heptane (4.0 ml), CO / H_2 (200 / 400 psi), 120 °C, 20 h.
b) Determined by GC.
c) Determined by GC and ^1H NMR.
d) 80 °C.
e) 100 °C.
f) No additional ligand. g) 30 h.



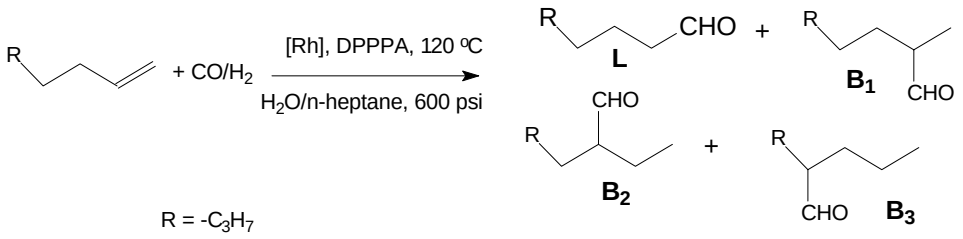
PEO-DPPPA (L) (n + m = 34)

600 psi of CO / H_2, the conversion increased from 80 % for CO / H_2 = 1/5 to 82 % for CO / H_2 = 1/2 and finally to 66 % for CO / H_2 = 2/1 (400 /200 psi). The conversion dropped to only 6 % when no additional ligand was used (Table 3.3, entry 6). The hydroformylation of a variety of alkenes occurred smoothly under the same conditions [120 ^oC, CO / H_2 (200 / 400 psi)] with the same catalyst and ligand. The hydroformylation of styrene usually leads to the branched aldehyde, 1-phenyl-1-propanal (**B**) (XXIII), and the linear aldehyde, 2-phenyl-1-propanal (**L**) (XXIV) (Eq. 2.1). The conversion of styrene increased from 64 % to 96 % and selectivity for the branched dropped from 72 % to 54 % for 80 ^oC and 120 ^oC, respectively (Table 3.3 entries 7,8). The thermoregulated phase transfer hydroformylation was successfully applied to higher olefin such as 1-hexadecene with a conversion of 74 % and selectivity toward the linear aldehydes of 48 %.

3.4.2 Thermoregulated phase transfer hydroformylation: Catalyst recycling.

Recycling experiments were designed to test the recycling efficiency of the catalyst. When the reaction was complete, the organic phase was separated from the reaction system by decantation and the catalyst remained in the aqueous phase. Then, a fresh organic solvent and substrate were added the catalyst can be recycled. Table 3.4 shows the results of the catalyst recycling in the thermoregulated phase transfer biphasic

Table 3.5. Thermoregulated regulated phase transfer hydroformylation: Recycling of the catalyst.[a]



Eq. 3.16

Entry	# of cycles	Catalyst	Conv.[b] %	Product distribution[c]			
				L %	B_1 %	B_2 %	B_3 %
1	1	$[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$	82	45	36	11	8
2	2	$[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$	66	50	35	9	6
3	3	$[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$	60	54	35	7	4
4	4	$[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$	60	55	35	6	4
5	5	$[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$	58	58	34	5	3
6	1[d]	$RhCl_3.3H_2O$	90	39	37	13	11
7	2[d]	$RhCl_3.3H_2O$	91	40	38	12	10
8	3[d]	$RhCl_3.3H_2O$	92	39	38	13	10
9	4[d]	$RhCl_3.3H_2O$	89	45	37	10	8
10	5[d]	$RhCl_3.3H_2O$	87	40	37	13	10
11	6[d]	$RhCl_3.3H_2O$	90	39	38	13	10

a) Reaction conditions: $[Rh(CO)(\mu\text{-imid})(DPPPA\text{-}PEO)]_2$ (0.005 mmol), DPPPA-PEO (0.01 mmol), 1-octene (5.0 mmol), H_2O (4.0 ml), n-heptane (4.0 ml), CO/H_2 (200/400 psi), 120 ^oC, 20 h.
b) Determined by GC with n-decane as internal standard.
c) Determined by GC and ^1H NMR.
d) 110 ^oC, 4.0 ml of Toluene in place of n-heptane, 8 h.

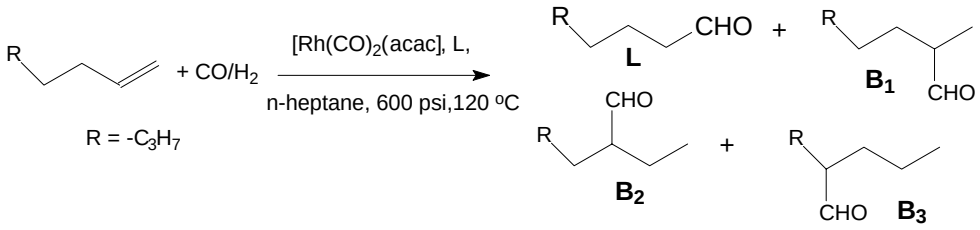
hydroformylation of 1-octene. The catalytic system based on [Rh(CO)(μ-imidazole)(DPPPA-PEO)]$_2$ / DPPPA-PEO / n-heptane / H_2O gave moderate conversion of (58 %) after recycling five times.

The catalyst generated in situ from $RhCl_3.3H_2O$ and DPPPA-PEO ligand, was also tested in the recycling experiments. The activity of this catalyst was better than the [Rh(CO)(μ-imidazole)(DPPPA-PEO)]$_2$, even when the reactions were carried out at lower temperature (110 ^oC) and at shorter reaction time (8 h) (Table 3.4, entries 6-11). After a catalyst recycling of six times, the conversions of 1-octene into aldehydes are still as high as 90 %. The reason for this higher catalytic activity could be explained by the fact that $RhCl_3.3H_2O$ is more soluble in water than the [Rh(CO)(μ-imidazole)(DPPPA-PEO)]$_2$ catalyst.

3.4.3 Thermoregulated phase-separable hydroformylation: Catalyst recycling

The strategy of thermoregulated phase-separable catalysis (TPSC) was developed using nonionic phosphine with the property of critical solution temperature (CST) that helps separating the ligand, recovering and reusing the rhodium homogeneous catalyst. Table 3.5 indicated the recycling efficiency of $Rh(CO)_2(acac)$ / DPPPA-PEO complex in the hydroformylation of 1-octene. After the reaction, the catalyst precipitated as a rose viscous wax from the reaction mixture on cooling to room temperature. The separated catalyst was reused up to five times without apparent decrease in activity. The catalyst generated in situ from $Rh(CO)_2(acac)$ and binaphtyl phosphite-PEO ligand was also tested in the recycling experiments (Table 3.5, entries 6-10).

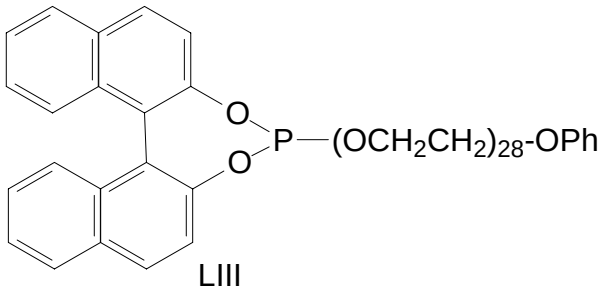
Table 3.6. Thermoregulated phase-separable hydroformylation: Recycling of the catalyst.[a]



Eq. 3.16

Entry	# of cycles	Ligand	Conv.[b] %	Product distribution[c]			
				L %	B_1 %	B_2 %	B_3 %
1	1	DPPPA-PEO	88	37	38	14	11
2	2	DPPPA-PEO	70	40	41	11	8
3	3	DPPPA-PEO	75	41	37	12	9
4	4	DPPPA-PEO	81	42	37	12	9
5	5	DPPPA-PEO	94	38	38	13	11
6	1[d]	Binapthyl phosphite-PEO	93	39	38	13	10
7	2[d]	Binapthyl phosphite-PEO	88	40	38	13	10
8	3[d]	Binapthyl phosphite-PEO	94	39	38	13	10
9	4[d]	Binapthyl phosphite-PEO	83	40	38	13	10
10	5[d]	Binapthyl phosphite-PEO	90	40	39	12	9

a) Reaction conditions: $Rh(CO)_2(acac)$ (0.005 mmol), DPPPA-PEO (0.02 mmol), 1-octene (5.0 mmol), n-heptane (8.0 ml), CO / H_2 (200 / 400 psi), 120 ^oC, 20 h.
b) Determined by GC with n-decane as internal standard.
c) Determined by GC and ^1H NMR.
d) 0.02 mmol of binapthyl phosphite-PEO was used in place of DPPPA-PEO



LIII

The activity of this catalyst and selectivity was similar to the activity of $Rh(CO)_2(acac)$ / DPPPA-PEO catalytic system. After recycling for five times, the conversion of 1-octene into aldehydes are still as high as 90 % and the selectivity for the linear was 40 %.

3.5 Mechanism

The FT-IR spectrum of a dichloromethane solution of the catalyst $HRh(CO)(PPh_3)_3$ (LIV) shows, after 30 minutes, a new band at 1978 cm^{-1} (figure 3.9a) which is attributed to the $[Rh(CO)(PPh_3)_2]_2$ (LV) in agreement with the known behavior (9,10). When the catalyst precursor solution was pressurized with 10 bars of CO at 298 K, the absorptions at 2008 and 1926 cm^{-1} characteristic of the precursor were replaced by the new peaks at 2041, 1981 and 1945 cm^{-1} (Figure 3.9b). The new bands can be attributed to $HRh(CO)_2(PPh_3)_2$ (LVI) in agreement with the data reported in the literature (121). Additional bands were also observed for $[Rh(PPh_3)_2(CO)_2]_2$ (LVII) complexes at around 2075 and 1816 cm^{-1} (Figure 3.9c) when the reaction is conducted without additional ligand (Figure 3.9c). This can be explained by the displacement of the ligand resulting in the formation of carbonyl clusters. The IR spectroscopy studies on rhodium carbonyl compounds like $[Rh_4(CO)_{12}]$ has revealed bands of 2080, 2050, 1860 cm^{-1} (97).

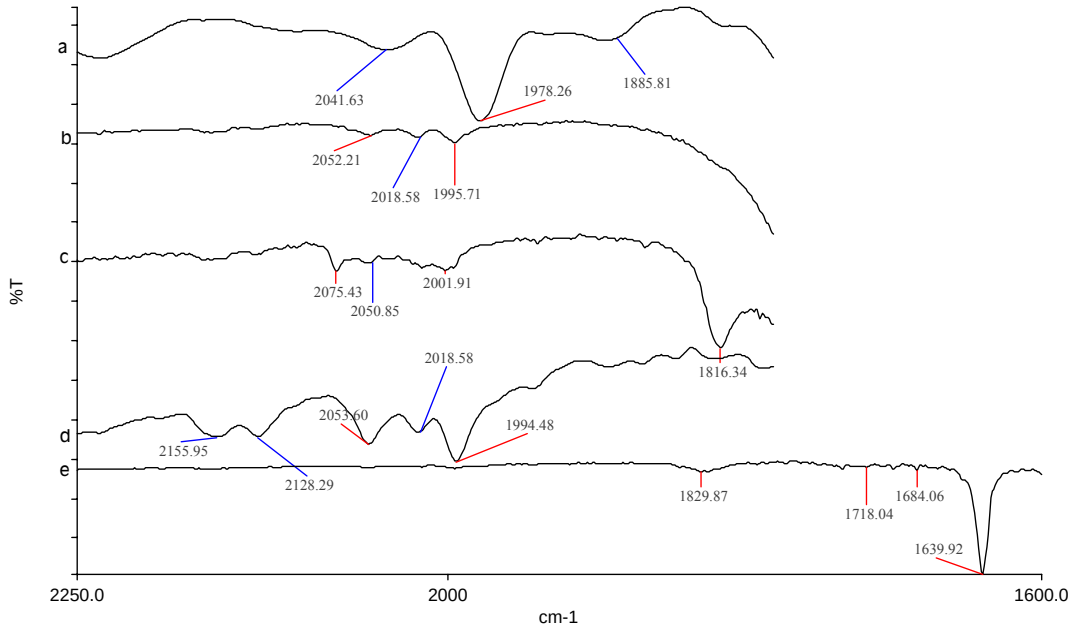
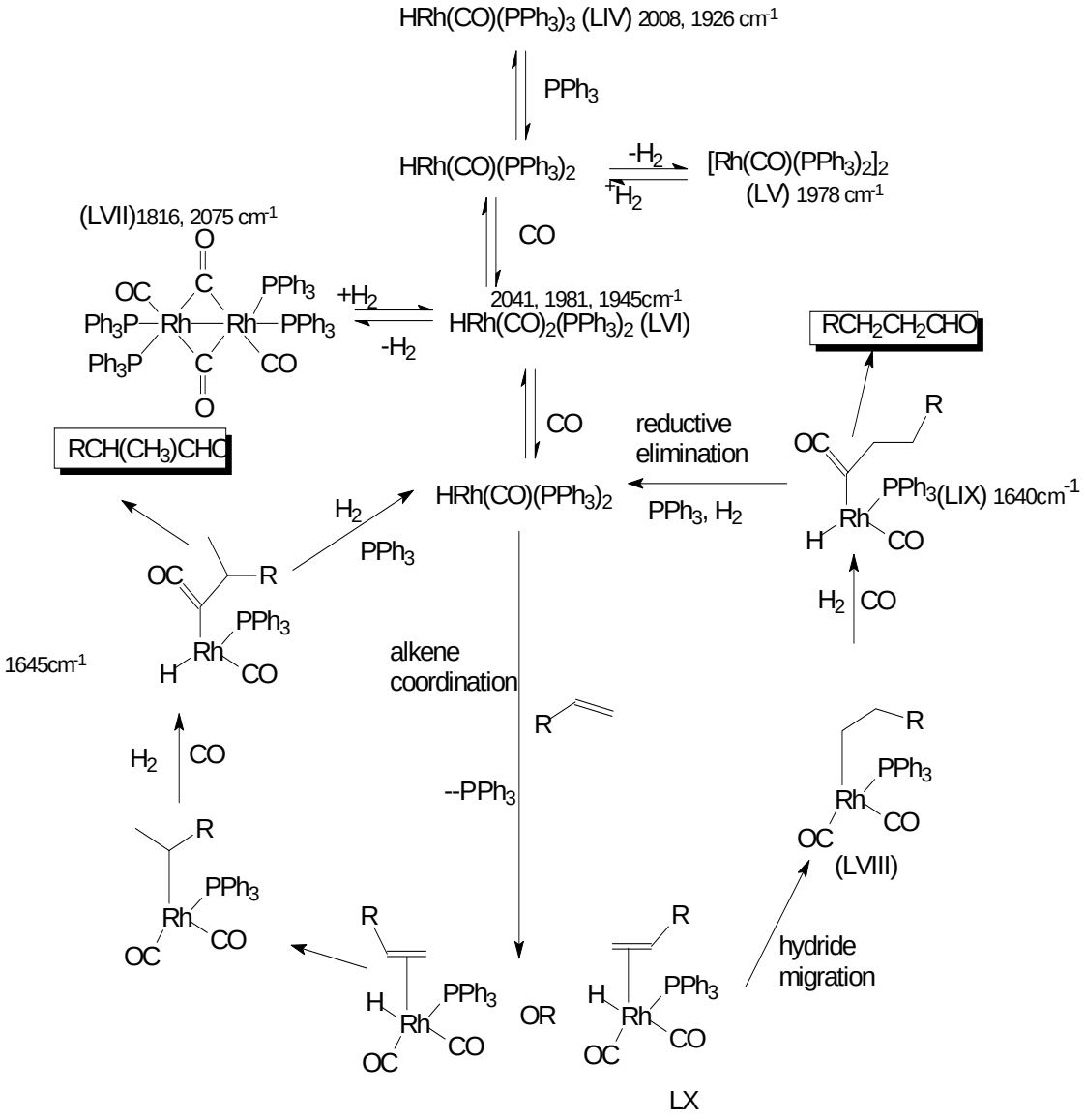


Figure 3.9. FT-IR spectra of : a) $HRh(CO)_2(PPh_3)_3$ 0.01mmol, 1.5 ml CH_2Cl_2; b) $HRh(CO)_2(PPh_3)_3$ 0.01mmol, 1.5 ml CH_2Cl_2, 0.03 mmol $P(OPh)_3$, 90 ^oC, 1 h, 1.0 mmol of 1-octene, CO/H_2 = 1 (200 psi); c) $HRh(CO)_2(PPh_3)_3$ 0.01mmol, 1.5 ml CH_2Cl_2, **no ligand,** 90^oC, 1 h, 1.0 mmol of 1-octene, CO/H_2 = 1 (200 psi); d) $HRh(CO)_2(PPh_3)_3$ 0.01mmol, 1.5 ml CH_2Cl_2, 0.03 mmol $P(OPh)_3$, 90 ^oC, 1 h, CO/H_2 = 1 (200 psi); **no substrate**; e) acyl intermediate $HRh(CO)_2(PPh_3)_3$ 0.01mmol, $P(OPh)_3$ (0.03 mmol), 1-octene (1.0 mmol), CO 100 psi, 1.5 ml CH_2Cl_2, 90 ^oC, 1 h, **no H_2**;

Proposed reaction mechanism for the biphasic hydroformylation



Scheme 3.3

The reaction of 1-octene with the catalyst precursor (LIV) in the presence of 100 psi of CO resulted to the formation of a broad band at around 1640 cm^{-1}, which is the region characteristic for the acyl group stretching (12), so could be assigned to acyl complex (LIX) (Figure 3.9e).

Following the CO dissociation from the $HRh(CO)_2(PPh_3)_2$ complexes, the regioselectivity in the hydroformylation will be determined by two consecutive steps of alkene coordination and hydride migration. van der Veen et. Al. (96) suggested that the regioselectivity is controlled by the alkene attack on the four-coordinate intermediate via a square-pyramidal transition state similar to structure LX (Scheme 3.3). Increasing cone angle of the phosphine in intermediate LX resulted in increased embracing of the rhodium center by the ligand and consequently in more steric hindrance for the alkene entering the coordination sphere.

3.6 Conclusion

The thermomorphic biphasic hydroformylation of 1-octene led to a very high conversion of alkenes and excellent yields of aldehydes and also a very attractive selectivity in the desired linear aldehydes. This selectivity depended mainly on the amount of $P(OPh)_3$, the total pressure of CO / H_2, the ratio of CO / H_2, the reaction time and the temperature. A variety of alkenes were converted into linear aldehydes at the optimum reaction conditions that included: $P(OPh)_3$ / [Rh] = 12, 90 ^oC, CO / H_2 =100/100 psi and 1.5 h. DMSO / n-heptane and PC / n-heptane solvents pair were highly efficient especially in the recycling process where excellent conversion and selectivities were maintained.

A novel non-ionic water soluble phosphine ligand DPPPA-PEO has been synthesized by two-step ethoxylation of DPPPA. This phosphine ligand demonstrates the

character of inverse temperature-dependant water solubility. The DPPPA-PEO catalyst formed in situ by $RhCl_3.3H_2O$ shows a high activity and excellent recycling efficiency in the aqueous-organic biphasic hydroformylation of 1-octene through the process of thermoregulated phase transfer catalysis.

CHAPTER 4

4.0 SUPPORTED RHODIUM CATALYZED HYDROFORMYLATION OF ARYL ALKENES

4.1 Introduction

Hydroformylation or Oxo process is an old and important industrial process for the production of oxygenates including aldehydes from olefins and syngas. It has been known that Cobalt and Rhodium catalysts are the most active in this process at the industrial level (1-3). While the industrially relevant products of hydroformylation were produced by the homogeneous systems over the past 20 years, the research work has continued actively to improve the catalysts activity and recycling (1-3). The immobilization or heterogenization of homogeneous catalysts on inorganic support materials was actively investigated and can be achieved by various methods (51,122,123). Rh/Al_2O_3 catalyst with high rhodium dispersion was active in the hydroformylation of styrene but it suffered from leaching (122). Immobilization of a dinuclear rhodium (II) acetato complex with bridging *ortho*-metalated phosphine ligands on MCM-41 resulted in useful catalysts for hydroformylation of styrene and 1-decene (57). A polysilicate immobilized rhodium complex was found to be a selective hydroformylation catalyst showing an overall selectivity for the linear aldehyde of 94.6 % with 1-octene at 80 °C and 50 atmosphere of CO / H_2 (1:1) (124). Functionalization of MCM-41 with 3-aminopropyltrimethoxysilane (APTS), and subsequent encapsulation and anchoring of $HRh(CO)(PPh_3)_3$ in the mesoporous material was reported as an active catalysts for the hydroformylation of 1-octene (51).

$Rh_4(CO)_{12}$ has been successfully anchored to MCM-41(PPh_2), MCM-41(NH_2) and MCM-41(SH), the effect of the three donor ligands on the catalytic hydroformylation of cyclohexene were compared (62). In recent years, the immobilization of Rh-PPh_3 complexes onto amino-functionalized MCM-41 and MCM-48 as efficient heterogeneous catalyst for higher olefin hydroformylation has been reported by several groups (63,64).

Another approach to immobilizing homogeneous catalysts on solid supports has been reported, in which the Wilkinson‘s hydroformylation catalyst complex was tethered through heteropolyacid to zeolites (61,65), this result to an excellent stability, reusability and even improved activity.

4.2. Experimental

4.2.1 General

All chemicals, otherwise stated, including solvents and alkenes were highly pure (> 99%) and were purchased from Sigma-Aldrich Company. The solvents used in the experiments, such as THF, hexane, cyclohexane, CH_2Cl_2, benzene, 1,4-dioxane, methyl ethyl ketone (MEK), acetone, 1,2-dimethoxyethane (DME), methanol, ethanol, and others were HPLC grade and were stored under nitrogen over activated 3Å molecular sieves. Anisole, tetraethoxysilane (TEOS), n-hexadecyltrimethyl ammonium (or cetyltrimethyl ammonium) bromide, ammonium hydroxide, tetramethyl ammonium bromide (25 % by weight solution in water), triphenylphosphite [$P(OPh)_3$] and $H_3PW_{12}O_{40}.25H_2O$ were used without any further purification. The rhodium complexes $RhCl_3.3H_2O$, $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, and $RhHCO(PPh_3)_3$ (Strem Company) were used without purification.

4.2.2 Preparation of MCM-41

MCM-41 having pore size 30 Å, used as a support for the impregnation of the catalysts, was synthesized according to the method described in literature (125). 2.5 g of n-hexadecyltrimethylammonium bromide (C_{16}TMABr, 0.007 mol) was dissolved in 50 g of deionized water, and 13.2 g of aqueous ammonia (32 wt %. 0.25 mol) and 60.0 g of absolute ethanol (EtOH, 1.3 mol) were added to the surfactant solution. The solution was stirred for 15 min (250 rpm) and 4.7 g of TEOS (0.022 mol) freshly distilled was added at one time resulting in a gel with the following molar composition: 1TEOS:0.3C16TMBr:11NH_3:144H_2O:58EtOH. After stirring for 2 h the white precipitate was filtered and washed with 100 ml of deionized water and 100 ml of methanol. After drying over night at 363 K, the sample was heated to 823 K (rate: 1 K per min^{-1}) in air and kept at that temperature for 5 h.

The MCM-41 samples was analyzed by X-ray diffraction using JOEL JDX-3530 diffractometer with Cu Kα radiation (λ = 0.15405 nm). Diffraction data were recorded between 1 and 30^o 2θ in steps of 0.02^0 with a count time of 1 s at each point. We assume that the wall thickness is 10 Å.

4.2.3 Preparation and Characterization of Rhodium (I) and Rhodium (III) Impregnated with and without Heteropolyacids on MCM-41

The MCM-41 materials with pore size of 30 Å were chosen as the inorganic support for the impregnation processes due to their large pore size and high specific surface area. In addition, the method of synthesis is easy, simple and fast compared to

MCM-41 (50 Å) with equivalent catalytic activity as a support in the hydroformylation tests. The catalytic systems obtained are designated:

Rh*n*mH**p**S**-*S***

Where: Rh (Rhodium Complex); *n* (Oxidation state); m (% Rhodium Impregnated); H (Type of the Heteropolyacid or ligand); p (% impregnation of HPA-n); S (Support); *S* (Solvent of impregnation).

4.2.4 Synthesis of 1-2% of Rh(I) or Rh (III) / HPA / MCM-41 in Methanol (M) or Water (W) [Rh32HPA10MCM-M (W)] and [Rh12HPA10MCM-M (W)]

$RhCl_3$. $3H_2O$ [or Rh (I) complexes] alone or with the co-catalyst was impregnated on the MCM-41 using methanol (M) or water (W) as a solvent. For example, a mixture solution of 2 % (11.4 mg) $RhCl_3$. $3H_2O$ and 10 % (56.8 mg) of $H_3PW_{12}O_{40}.25H_2O$ (HPA-W_{12}) were stirred for 30 minutes at room temperature under nitrogen atmosphere. 500 mg of MCM-41 were than added to the homogeneous solution and mixture was stirred for 24 h. The solvent was removed under vacuum and the solid sample was dried at 90 ^oC for 2 h and stored in the refrigerator. The catalysts prepared are summarized in Tables 4.1.

4.2.5 Synthesis of 5 % of Rh (I) or Rh (III) / HPA/MCM-41 in ethanol (E) [Rh35HPA10MCM-E] and [Rh15HPA10MCM-E]

The tethered catalyst was prepared following the procedure reported by Augustine and co-workers (60). 33 μmol of HPA dissolved in 20 ml of ethanol and 500 mg of

MCM-41, the solution was stirred at room temperature for 16 h, the resulting solid was filtered and washed with ethanol to remove HPA and finally dried at 100 ^{o}C for 6 h.

The solid was suspended in 20 ml dry ethanol and 30 μmol $HRhCO(PPh_3)_3$ was added and refluxed (at 80 ^{o}C) under stirring for 18 h. The light gray solid product was then washed with ethanol repeatedly to remove unanchored to HPA, dried at 80 ^{o}C and used as such for the reaction. The catalysts prepared are summarized in Tables 4.1.

4.2.6 Impregnation of rhodium (I) or rhodium (III) with and without heteropolyacid on MCM-41

The impregnation of the rhodium complexes was realized on MCM-41 (30 Å) and MCM-41 (50 Å). Tables 4.1 summarize the most important supported catalysts prepared by impregnation of 2 % of $RhCl_3$. $3H_2O$, with and without 10 % of the heteropolyacid $H_3PW_{12}O_{40}$ (HPA-W_{12}) in methanol (Catalysts No. Rh-1: RhW-4) or in water as a solvent (catalysts No. Rh-5 and RhW-6) on MCM-41 (30 Å). In addition, $RhCl_3$. $3H_2O$ (2 %) was impregnated with HPA-W_{12} (10 %) on MCM-41 (50 Å) in dry methanol as a solvent (catalyst No. Rh-7). Another heteropolyacid such as $H_3PMo_{12}O_{40}$ was considered with $RhCl_3$. $3H_2O$ for the impregnation on MCM-41 (30 Å) (catalyst No. RhMo-8). 5 % of $RhCl_3$. $3H_2O$ were also impregnated with and without HPA-W_{12} or HPA-Mo_{12} on MCM-41 (30Å) in dry ethanol as a solvent of impregnation (catalysts No. Rh-9: RhMo-11). Similarly, the rhodium (I) complex $[Rh(COD)Cl]_2$ (**Rh^{A}**) (2 %) was impregnated on MCM-41 (30Å) and MCM-41 (50 Å) with and without HPA-W_{12} (10%) in dry methanol as a solvent (catalysts No. Rh-12: RhW-14). Other rhodium (I) complexes such as $[Rh(CO)_2Cl]_2$ (**Rh^{B}**) and $HRhCO(PPh_3)_3$ (**Rh^{C}**) were impregnated on MCM-41 (30 Å) in a similar manner (catalysts No. Rh-15 : RhW-18) in dry methanol. The other

Table 4.1. Supported catalysts obtained by impregnation of Rhodium (III) and rhodium (I) with and without Heteropolyacid (HPA-n).

Catalyst No.	Catalyst	Rhodium %	HPA-n (H) / Co-catalysts %	MCM-41 Å	Solvent (S)
Rh-1	**Rh*3*2MCM-*M***	$Rh^{III}Cl_3, 3H_2O$ 2 %	-	30 Å	Methanol (*M*)
RhW-2	**Rh*3*2W5MCM-*M***	$Rh^{III}Cl_3, 3H_2O$ 2 %	$H_3PW_{12}O_{40}$ 5 %	30 Å	Methanol (*M*)
RhW-3	**Rh*3*2W10MCM-*M***	$Rh^{III}Cl_3, 3H_2O$ 2 %	$H_3PW_{12}O_{40}$ 10 %	30 Å	Methanol (*M*)
RhW-4	**Rh*3*2W20MCM-*M***	$Rh^{III}Cl_3, 3H_2O$ 2 %	$H_3PW_{12}O_{40}$ 20 %	30 Å	Methanol (*M*)
Rh-5	**Rh*3*2MCM-*W***	$Rh^{III}Cl_3, 3H_2O$ 2 %	-	30 Å	Water (*W*)
RhW-6	**Rh*3*2W10MCM-*W***	$Rh^{III}Cl_3, 3H_2O$ 2 %	$H_3PW_{12}O_{40}$ 10 %	30 Å	Water (*W*)
RhW-7	**Rh*3*2W10MCM'-*M***	$Rh^{III}Cl_3, 3H_2O$ 2 %	$H_3PW_{12}O_{40}$ 10 %	50 Å	Methanol (*M*)
RhMo-8	**Rh*3*2Mo10MCM-*M***	$Rh^{III}Cl_3, 3H_2O$ 2 %	$H_3PMo_{12}O_{40}$ 10 %	30 Å	Methanol (*M*)
Rh-9	**Rh*3*5MCM-*E***	$Rh^{III}Cl_3, 3H_2O$ 5 %	-	30 Å	Ethanol (*E*)
RhW-10	**Rh*3*5W10MCM-*E***	$Rh^{III}Cl_3, 3H_2O$ 5%	$H_3PW_{12}O_{40}$ 10 %	30 Å	Ethanol (*E*)
RhMo-11	**Rh*3*5Mo10MCM-*E***	$Rh^{III}Cl_3, 3H_2O$ 5%	$H_3PMo_{12}O_{40}$ 10 %	30 Å	Ethanol (*E*)
Rh-12	**Rh^{A}*1*2MCM-*M***	$[Rh^{I}(COD)Cl]_2$ 2 %	-	30 Å	Methanol (*M*)
RhW-13	**Rh^{A}*1*2W10MCM-*M***	$[Rh^{I}(COD)Cl]_2$ 2 %	$H_3PW_{12}O_{40}$ 10 %	30 Å	Methanol (*M*)
RhW-14	**Rh^{A}*1*2W10MCM'-*M***	$[Rh^{I}(COD)Cl]_2$ 2 %	$H_3PW_{12}O_{40}$ 10 %	50 Å	Methanol (*M*)
Rh-15	**Rh^{B}*1*2MCM-*M***	$[Rh(CO)_2Cl]_2$ 2 %	-	30 Å	Methanol (*M*)
RhW-16	**Rh^{B}*1*2W10MCM-*M***	$[Rh(CO)_2Cl]_2$ 2 %	$H_3PW_{12}O_{40}$ 10 %	30 Å	Methanol (*M*)
Rh-17	**Rh^{c}*1*2MCM-*M***	$HRhCO(PPh_3)_3$ 2 %	-	30 Å	Methanol (*M*)
RhW-18	**Rh^{c}*1*2W10MCM-*M***	$HRhCO(PPh_3)_3$ 2 %	$H_3PW_{12}O_{40}$ 10 %	30 Å	Methanol (*M*)
RhMo-19	**Rh^{A}*1*2Mo10MCM-*M***	$[Rh^{I}(COD)Cl]_2$ 2 %	$H_3PMo_{12}O_{40}$ 10 %	30 Å	Methanol (*M*)
Rh-20	**Rh^{c}*1*5MCM-*E***	$HRhCO(PPh_3)_3$ 5 %	-	30 Å	Ethanol (*E*)
RhW-21	**Rh^{c}*1*5W10MCM-*E***	$HRhCO(PPh_3)_3$ 5 %	$H_3PW_{12}O_{40}$ 10 %	30 Å	Ethanol (*E*)
RhMo-22	**Rh^{c}*1*5Mo10MCM-*E***	$HRhCO(PPh_3)_3$ 5 %	$H_3PMo_{12}O_{40}$ 10 %	30 Å	Ethanol (*E*)

heteropolyacid $H_3PMo_{12}O_{40}$ was also considered with $[Rh(COD)Cl]_2$ (**Rh^A**) for the impregnation on MCM-41 (30 Å) (catalyst No. RhMo-19). It is important to note that $Rh_6(CO)_{16}$ was not considered for impregnation due to the very low solubility in methanol or water at room temperature and even at 60 ^oC. 5 % of $RhHCO(PPh_3)_3$ were also impregnated with and without HPA-W_{12} or HPA-Mo_{12} on MCM-41 (30 Å) in dry ethanol as a solvent of impregnation (catalysts No. Rh-20: RhMo-22).

4.2.7 Characterization of Supported Catalyst

4.2.7.1 Infrared

The IR spectrum of the Rhodium complex $HRh(CO)(PPh)_3$ showed bands at 1921 cm^{-1} and 512 cm^{-1} for Rh–CO, and Rh–P respectively. However, after its impregnation on MCM-41 giving Rh*12*MCM-*M*, the Rh–CO shifted to 1942 cm^{-1} (Figure 4.1c). When the same catalyst was treated with 600 psi of CO / H_2 for two hours at 110 ^oC, two peaks appeared at 2013 and 2083 cm^{-1} which probably correspond to two gem carbonyl functions, which confirms the replacement of PPh_3 ligand by CO. Similar assignments were also made in previous workers (63,126,127) (Figure 4.1a).

After the hydroformylation reaction of styrene, two new bands were observed to develop at 2040 and 1661 cm^{-1}. The two peaks are tentatively attributed to Z-O-$RhCO(PhCHCH_2)$ and Z-O-$Rh(Ph(CH_3)COCH_3)$ (Z=support), respectively (128).

However, all the catalyst at the end of several cycles has an additional new absorption, at 1712 cm^{-1}. It occurs in a frequency range characteristic of Rh–CO–Rh bridging with C–O stretching. This datum logical requires that, in the species giving rise to the 1712 cm^{-1} band, two Rh centers be less than ≤3 Å apart (129) (Figure 4.1c).

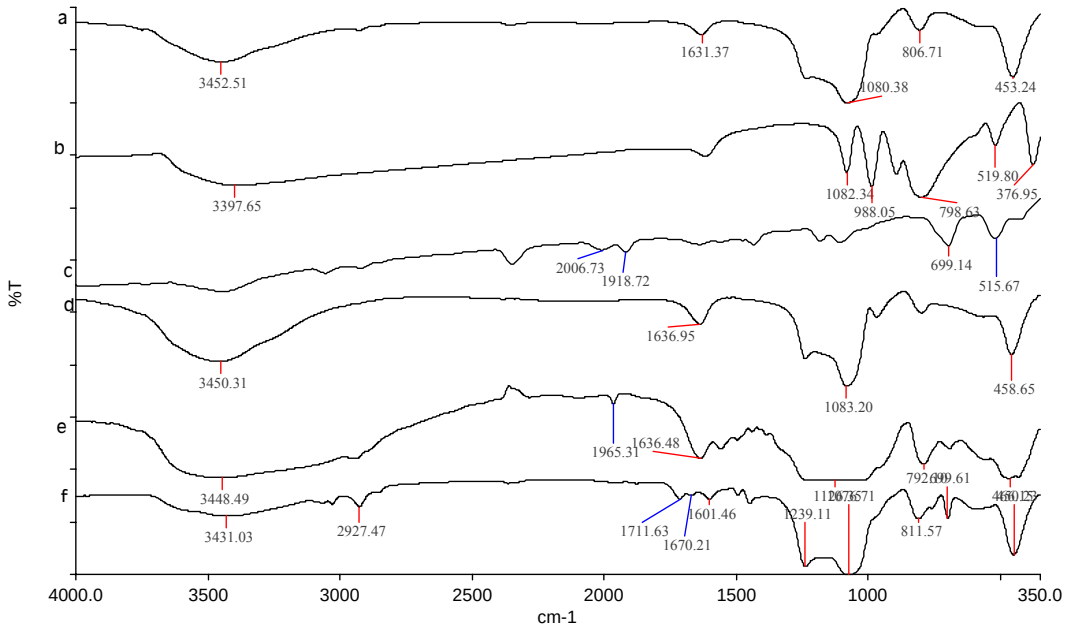


Figure 4.1. FT-IR spectra of different materials a) MCM-41; b) HPW_{12}; c) $HRhCO(PPh_3)_3$; d) MCM-41/HPW_{12}; e) **Rh^{B}*15*W10MCM-*E***; f) Recycled supported catalyst **Rh^{B}*15*W10MCM-*E*** after 6 cycles.

4.2.7.2 ^{29}Si MAS NMR

Spectra of W*10*MCM-41 and Rh*15*W*10*MCM-E at 99.44 MHz revealed almost no variation in the Q^3 ($(SiO_3)_3$≡Si-OH) and Q^4 ($(SiO)_3$≡Si-O-Si≡) chemical shifts (δ =-100 ppm and δ =-110 ppm, respectively) although, there was a substantial change observed in the Q^3/Q^4 ratio. A possible reason for the lower value of Q^3/Q^4 might be the decrease in the population of free silanol group due to the linkage arising from anchoring with HPA (51) (Appendix Figure A4.1).

4.2.7.3 ^{31}P CP-MAS NMR

The catalyst was characterized using ^{31}P CP-MAS NMR. The spectra of $HRh(CO)(Ph_3)_3$ complex have earlier been reported (51,65) to have two major peaks (δ_{iso} 34.4, 45.4 ppm) (Appendix Figure A4.2), each split by J-coupling to other ^{31}P and ^{103}Rh (natural abundance of 100%) nuclei. The spectra pattern observed in $HRh(CO)(PPh_3)_3$ thus elucidated the trigonal bipyramidal structure of the complex. The results of the ^{31}P spectra of HPA-W_{12} and rhodium complex, Rh*15*W*10*MCM-*E* showed a totally different spectrum with peaks (δ_{iso} 31.23 & 45.36 ppm). This shift in the NMR spectrum of Rh*15*W*10*MCM-*E* catalyst may be due to the interaction of HPA-W_{12} and $HRh(CO)(PPh_3)_3$ tethered to MCM-41 matrix, where Rh-O-W-O-Si type of bond formation may have taken place (65).

4.2.7.4 XRD

The catalysts materials (mesoporous phases of MCM-41, HPA-MCM-41, Rh-HPA-MCM-41 and Rh-HPA-MCM-41 catalysts after various recycles) were characterized and analyzed by powder XRD patterns and also the pore diameters were

calculated. Bragg peaks were indexed assuming a hexagonal symmetry and pore wall thickness of 10 Å. The pore diameters can be approximated by the formula:

$$(2/(3)^{1/2})d_{100} - 10Å$$

The distinct reflection and crystallinity or morphology (determined by the peak positions) remains unaltered from one another, as observed by the powder XRD. This shows that there is no change in crystallinity or morphology of MCM-41 embedded with HPA compared to that of the neat MCM-41 and the porous framework the Rh-HPA-MCM-41 catalyst was not affected or damaged during the complex formation (Appendix Figure A 4.3).

4.2.7.5 Nitrogen adsorption-desorption isotherms

The measurement of the nitrogen adsorption isotherms is very useful for the assessment of the properties of the MCM-41 materials. The MCM-41 were characterized against the specific surface area and the pore volume using the adsorption-desorption isotherms of nitrogen obtained at 77 K on a Quantachrome Autosorb 6B (NOVA-1200 BET surface area analyzer). The samples were out-gassed at 423 K and 1 MPa for 12 h before measurement were performed. The specific surface area of the MCM-41 (30 Å) and MCM-41 (50 Å) were 1007 m^2/g and 591m^2/g, respectively.

The adsorption-desorption isotherms of nitrogen of MCM-41 (30 Å) and **Rh^c*1***5**W**10**MCM**-*E* are given on the (Appendix Figure A4.4, and A4.5), respectively. At the adsorption branch, the adsorbed amount increased gradually with an increase in relative pressure by multilayer adsorption. A sudden uptake of the adsorbate was observed

over a narrow range of relative pressure (P/P_0) between 0.25 and 0.4 caused by capillary condensation of nitrogen in the mesopores. The branch of desorption of the isotherm coincides with adsorption branch. The sorption isotherms for MCM-41 (30 Å) and **Rh^{c}*1*5W10MCM-*E*** are in accord with those described in the literature (125,130).

4.2.7.6 Elemental analysis

The analysis of the percentage loading of rhodium (% Rh) and tungsten (% W) or molybdenum (% Mo) were carried out by ICP. The results are presented in (Appendix Table A4.1).

4.2.8 General procedure for the Heterogeneous hydroformylation of styrene

The following general procedure was considered for styrene, adopted as model substrates for aryl alkenes in the hydroformylation reaction. 50 mg or 20 mg of the supported catalyst were weigh into a glass liner equipped with magnetic bar. 5.0 ml of dry solvent added to the liner. 5.0 mmol (= 0.5208 g) of styrene or 5.0 mmol was added, and the liner placed into 25 ml high-pressure Parr autoclave. The autoclave was flushed thoroughly three times with carbon monoxide, subsequently pressurized with 300 psi of CO and 300 psi of hydrogen. The autoclaves were heated on hotplates controlled by temperature sensor to maintain the temperature constant (± 0.5 ^{o}C). The rate of stirring was maintained at 750 rpm. After the reaction time elapses, the autoclave was cooled to room temperature and the gas carefully released under fume hood. The reaction mixture was centrifuged twice to separate the solid catalyst from the liquid products. The solid catalyst was dried in oven at 60 ^{o}C and used again in another catalytic cycle. 100 μg of anisole were added to mixture as internal standard to determine the conversion of styrene.

The products were identified using GC, GC-MS, ^{1}H NMR and ^{13}C NMR techniques. The ratio of branched **(B)** to linear aldehydes **(L**) was determined by GC and ^{1}H NMR.

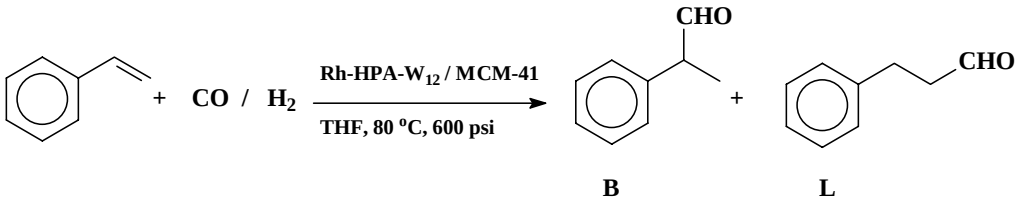
4.3 Results and discussion

The heterogeneous hydroformylation reaction represents an attractive industrial route for the production of aldehydes due to the relatively easy separation of products and high turnover of the rhodium catalysts. Many heterogeneous catalytic systems have been described in the literature, but to our knowledge, the combination of the heteropolyacids as co-catalysts with the rhodium (I) or rhodium (III) complexes as catalysts impregnated on MCM-41 has not been yet well explored in the hydroformylation of alkenes.

4.3.1 Rhodium (III) Supported Catalysts in the Heterogeneous Hydroformylation of Styrene.

MCM-41 was chosen as inorganic support due to its high surface area and large pore size. $RhCl_3.3H_2O$ (1-2 %) impregnated alone or with $H_3PW_{12}O_{40}$ (HPA-W_{12}) (5-20 %) on MCM-41 have been studied in the hydroformylation of styrene (Table 4.2). The conversions and the product distribution were monitored at 6 h and 16 h of the reaction. Rh32MCM-M and Rh32W10MCM-M gave no reaction in the absence of water (Table 4.2, entries 3,6). However, Rh32MCM-M catalyzed successfully the hydroformylation of styrene in the presence of 25 ml of water. The conversions were 36 % at 6h and 76 % at 16h of the reaction (Table 4.2, entries 1-2). The catalyst Rh32W10MCM-M gave excellent conversion equals to 98 % at 16 h compared to 76 % conversion at 6 h but only in the presence of 25 ml of water (Table 4.2, entries 4, 5). It was clear at this stage that the presence of water was essential for the occurrence of the reaction at 80 ^{o}C. The catalysts

Table 4.2 Rhodium (III) supported catalysts in the heterogeneous hydroformylation of styrene.[a]



Eq. 4. 1

Entry	Catalyst	Time h	Conversion[b] %	Product Distribution[c] %	
				B	L
1	**Rh*3*2MCM-*M***	6	36	71	29
2	**Rh*3*2MCM-*M***	16	76	70	30
3[d]	**Rh*3*2MCM-*M***	16	0	-	-
4	**Rh*3*2W10MCM-*M***	6	74	71	29
5	**Rh*3*2W10MCM-*M***	16	98	69	31
6[d]	**Rh*3*2W10MCM-*M***	16	0	-	-
7	**Rh*3*2MCM-*W***	16	65	73	27
8	**Rh*3*2W10MCM-*W***	16	92	71	29
9	**Rh*3*2Mo10MCM-*M***	6	Traces	-	-
10	**Rh*3*2Mo10MCM-*M***	16	11	74	26
11[e]	**Rh*3*2W10MCM-*M***	6	16	80	20
12[e]	**Rh*3*2W10MCM-*M***	16	46	78	22
13	**Rh*3*2MCM'-*M***	16	28	72	28
14	**Rh*3*2W10MCM'-*M***	16	77	76	24

a) Reaction conditions: catalyst (10 mg), Styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO / H_2 = 1/1), H_2O (25 µl = 1.39 mmol), 80 °C.
MCM= MCM-41 (30 Å), MCM'=MCM-41 (50 Å).
b) Determined by GC.
c) Determined by GC and ^{1}H NMR.
d) No water was used.
e) PPh_3 (0.04 mmol) was added into the liquid phase.

Rh32MCM-W and **Rh32W10MCM-W**, formed by the impregnation of rhodium (III) and the heteropolyacid in water, gave slightly lower conversions of styrene (Table 4.2, entries 7-8).

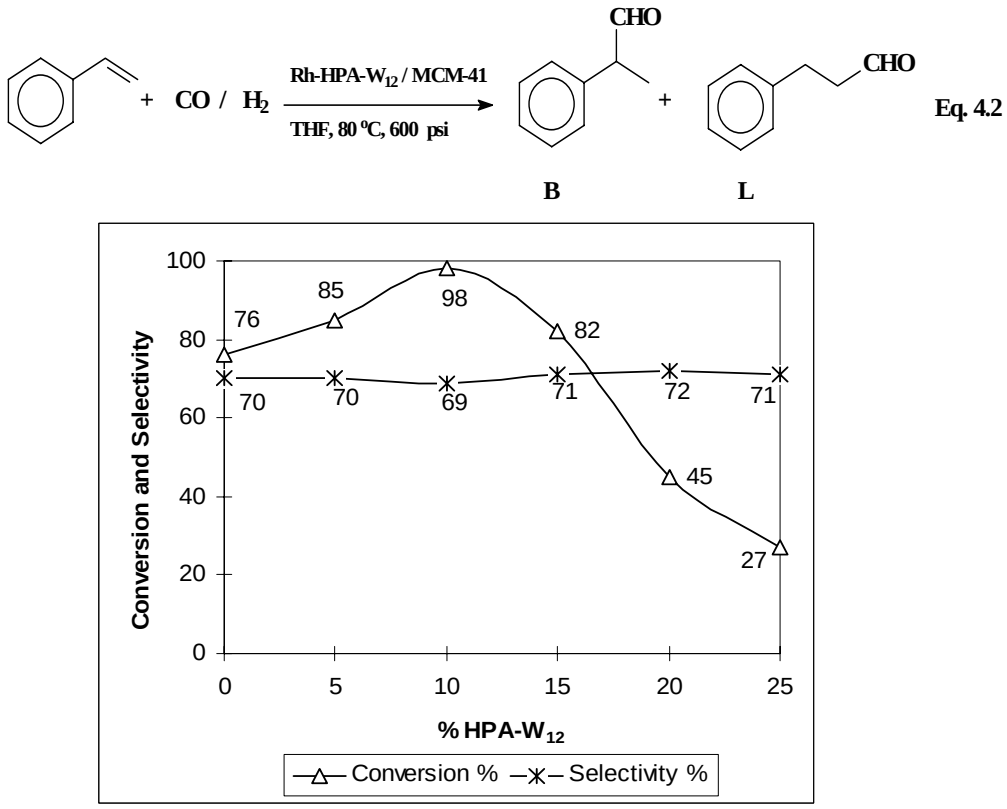
Interestingly, when $H_3PMo_{12}O_{40}$ was used instead of the HPA-W_{12} in the impregnation process with rhodium (III), we were surprised to observe that the supported catalyst seriously inhibited the reaction of hydroformylation of styrene (Table 4.2, entries 9-10); only 11 % of conversion was obtained after 16 h. The selectivity was slightly improved (78-80 %) toward the branched aldehyde (B) but the conversions dropped in a significant manner to 16 % at 6 h and 46 % at 16 h of the reaction. The use of the larger pore size support such as MCM-41 (50 Å) showed again the same advantages of MCM-41 (30 Å) of the impregnation of the rhodium (III) complex combined with HPA-W_{12} compared to the rhodium complex impregnated alone on the support (Table 4.2, entries 13-14). **Rh**32MCM'-M (2 % of $RhCl_3.3H_2O$ supported on MCM-41) gave 28 % of conversion after 16 h compared to 77 % with the catalysts Rh32W10MCM'-M prepared by supporting 2 % of $RhCl_3.\ 3H_2O$ and 10 % of HPA-W_{12} on MCM-41 (50 Å).

When the catalyst **Rh**32W5MCM-M formed of 2 % of $RhCl_3.3H_2O$ and impregnated with 5 % of HPA-W_{12} on MCM-41 in methanol, was used in the hydroformylation of styrene, the conversion was improved to 48 % at 6 h and 85 % at 16 h of the reaction (Figure 4.2) The increase of the percentage of loading of HPA-W_{12} from 10 % to 25 % (15 %, 20 %, and 25 %) and fixing the percentage of rhodium at 2 % decreased the conversions of the reaction from 98 % to 27 % (82 %, 45 %, and 27 %, respectively) (Figure 4.2). The selectivity toward the branched aldehyde was independent of the % loading and was obtained almost the same in all experiments.

The results, summarized in the Table 4.2 and Figure 4.3 showed the advantages of the use of the mesoporous materials, such as MCM-41, as supports for the impregnation of rhodium catalysts for the hydroformylation reactions. In addition, the combination of both $RhCl_3$. $3H_2O$ (2 %) and HPA-W_{12} (10 %) in the presence of water strongly enhanced the catalytic activity of the rhodium catalyst in the hydroformylation of styrene.

4.3.2 Rhodium (I) Supported Catalysts in the Heterogeneous Hydroformylation of Styrene.

Similar to the previous study, we have explored the supported catalysts obtained by the impregnation of rhodium (I) complexes combined to HPA-W_{12} and phosphine ligands on MCM-41 (30 Å) as a support. The results are summarized in the Table 4.3. Among rhodium (I) complexes, $[Rh(COD)Cl]_2$ (denoted as Rh^A) was supported with and without HPA-W_{12} on MCM-41. The catalyst Rh^A12MCM-M, obtained by the impregnation of 2 % of the rhodium (I) complex Rh^A alone on the mesoporous support, catalyzed the hydroformylation of styrene with conversions of 43 % at 6h and 76 % at 16 h (Table 4.3, entries 1-2). A significant improvement in the conversion of styrene with the catalyst Rh^A12W10MCM-M, formed by the impregnation 2 % of Rh^A and 10 % of HPA-W_{12} on MCM-41 was noticed. The conversion increased to 70 % at 6 h and to 97 % at 16 h with the selectivity toward branched aldehyde (B) maintained almost the same (71-72 %) (Table 4.3, entries 3-4). Another rhodium (I) complex $[Rh(CO)_2Cl]_2$ (denoted as Rh^B)



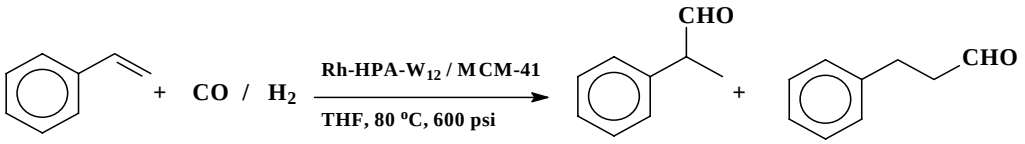
Eq. 4.2

Figure 4.2. Hydroformylation of styrene. Effect of % loading of HPA-W_{12}. Reaction conditions: % loading of Rhodium (2%), styrene (0.5208 g = 5.0 mmol), THF (5 ml), H_2O (25 μl = 1.39 mmol), CO (300 psi), H_2 (300 psi), 80 ^oC, 16 h.

was also considered in the impregnation process with and without HPA-W_{12} (2 % rhodium complex and 10% HPA-W_{12}) to give the catalysts **Rh**^{B}12MCM-M and Rh^{B}12W10MCM-M. The results of the catalytic hydroformylation tests with these two catalysts (Table 4.3, entries 5-8) were similar to those obtained with Rh^{A} based catalysts, but the catalytic activity of the catalysts obtained with Rh^{A} was slightly higher. Surprisingly, the rhodium catalyst $HRhCO(PPh_3)_3$ (denoted Rh^{C}) impregnated alone on MCM-41 in methanol gave a supported catalyst that was not very active in the hydroformylation of styrene. Only traces of products were obtained after 6 h of reaction and the conversion increased to 20 % after 16 h (Table 4.3, entries 9-10). It is clear that the reaction was very slow and went through a prolonged induction period.

However, the activity of the catalyst obtained from the impregnation of 2 % of Rh^{C} with 10 % of HPA-W_{12} was much higher; the conversion reached 71 % after 6 h and 95 % after 16 h (Table 4.3, entries 11-12). It seems that a very active intermediate complex was formed between Rh^{C} and HPA-W_{12} at the surface of the support. However, the small amount of the impregnated catalyst and probably the instability of the active rhodium intermediate species made the identification and the characterization of these species difficult. In order to improve the selectivity of the reaction, we have designed some experiments for which 10 mg of the catalyst Rh^{A}12MCM-M and 0.02-0.08 mmol PPh_3 were added in THF (Table 4.3, entries 13-14). The conversions were low (45-53 %). The use of another mesoporous material such MCM-41 (50 Å) as a support did not show a better catalytic activity for the catalyst Rh^{A} impregnated with HPA-W_{12} (Table 4.3, entry 15); the conversion of the reaction was 74 %. In order to study the recycling process and the characterization of the catalyst, another catalyst has been prepared by impregnating

Table 4.3. Rhodium (I) supported catalysts in the heterogeneous hydroformylation of Styrene.[a]



Eq. 4.3

B L

Entry	Catalyst	Times (h)	Conversion[b] %	Product Distribution[c] %	
				B	L
1	**Rh^{A}*1*2MCM-*M***	6	43	73	27
2	**Rh^{A}*1*2MCM-*M***	16	76	72	28
3	**Rh^{A}*1*2W10MCM-*M***	6	70	72	28
4	**Rh^{A}*1*2W10MCM-*M***	16	97	71	29
5	**Rh^{B}*1*2MCM-*M***	6	51	71	29
6	**Rh^{B}*1*2MCM-*M***	16	82	70	30
7	**Rh^{B}*1*2W10MCM-*M***	6	71	70	30
8	**Rh^{B}*1*2W10MCM-*M***	16	95	71	29
9	**Rh^{C}*1*2MCM-*M***	6	Traces	-	-
10	**Rh^{C}*1*2MCM-*M***	16	20	80	20
11	**Rh^{C}*1*2W10MCM-*M***	6	45	75	25
12	**Rh^{C}*1*2W10MCM-*M***	16	85	72	28
13[d]	**Rh^{A}*1*2MCM-*M***	16	53	74	26
14[e]	**Rh^{A}*1*2MCM-*M***	16	45	76	24
15	**Rh^{A}*1*2W10MCM'-*M***	16	74	72	28
16	**Rh^{C}*15W10*MCM-E**	16	95	78	22

a) Reaction conditions: catalyst (10 mg), styrene ((0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C, MCM= MCM-41 (30 Å), MCM'= MCM-41 (50 Å).
b) Determined by GC.
c) Determined by GC and ^1H NMR.
d) PPh_3 (0.04 mmol) was initially added into the liquid phase.
e) PPh_3 (0.08 mmol) was initially added into the liquid phase.

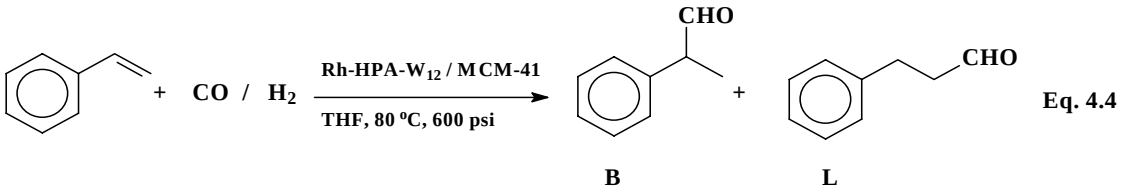
5 % of $HRhCO(PPh_3)_3$ (denoted Rh^C) with 10 % of HPA-W_{12} on MCM-41 in ethanol as a solvent of impregnation. The resulting supported catalyst Rh^C15W10MCM-E showed high catalytic activity (Table 4.3, entry 16). The study of the hydroformylation reaction catalyzed by supported rhodium (I) catalysts on MCM-41 showed high sensitivity toward the water where no conversion of styrene was observed in the presence of water.

Another class of rhodium catalysts with higher load (5 %) of rhodium have been prepared and tested in the hydroformylation of styrene. For example, **Rh***15*MCM-E, and **Rh***15*W*10*MCM-E and **Rh***15*Mo*10*MCM-E, which was prepared by refluxing 5 % of $HRhCO(PPh_3)_3$ in MCM-41 functionalized by HPA-W_{12} and HPA-Mo_{12} in ethanol, were evaluated for their activity and selectivity in hydroformylation of styrene. Different amount of catalyst (20-50 mg) were also used the catalytic run. The catalyst based on rhodium (III), **Rh***35*Mo*10*MCM-E, was also considered for comparison. The results are summarized in the Table 4.4. High conversions (94-99 %) were obtained at 110 ^oC after 3-6 h in cyclohexane as a solvent. However, the selectivity of the reaction was relatively lower (B / L = 1.3). The low selectivity is related to the high temperature of the reaction, which is a well known phenomenon in the chemistry of the hydroformylation.

4.3.3 Hydroformylation of Styrene. Effect of the amount of water on Rh(III) based catalysts

The addition of water into the liquid phase of the reaction catalyzed by **Rh***3*2**W**10**MCM**-*M*, obtained by the impregnation of $RhCl_3.3H_2O$ with HPA-W_{12} on MCM-41, has an enormous influence on the hydroformylation of styrene (Figure 4.3). The amount of water added to the mixture was also critical to the occurrence of the

Table 4.4. Heterogeneous hydroformylation of styrene. Effect of the type of catalyst based on Rhodium (I) or rhodium (III).[a]



Eq. 4.4

Run	Catalyst (mg)	Time h	Conversion[b] %	Product Distribution[c] %	
				B	L
1	**Rh*15*Mo*10*MCM-E (50 mg)**	3	97	57	43
2	**Rh*15*W*10*MCM-E (50 mg)**	3	97	59	41
3	**Rh*15*MCM-E (50 mg)**	3	99	54	46
4	**Rh*35*Mo*10*MCM-E (50 mg)**	6	98	58	42
5	**Rh*15*Mo*10*MCM-E (20 mg)**	6	98	63	37
6	**Rh*15*MCM-E (20 mg)**	6	99	86	14
7	**Rh*15*Mo*10*MCM-E (20 mg)**	6	94	61	39
8	**Rh*15*MCM-E (20 mg)**	6	97	60	40

a) Styrene (0.5208 g = 5.0 mmol), THF (5 ml), 600 psi (CO / H_2 = /1), cyclohexane (5.0 ml), 110 ^{o}C. MCM = MCM-41 (30 Å).
b) Determined by GC.
c) Determined by GC and ^{1}H NMR.

reaction. Only 15 % of the conversion was achieved in the absence of water after 6 h. The conversion increased to 60 % and 70 % with the addition of 5 µl and 10 µl of water, respectively. The Figure 4.2 has a maximum conversion of 74 % obtained with 25 µl of water. Interestingly, the increase in the amount of water led to a serious decrease of the conversion of styrene to reach 40 % with 100 µl of water.

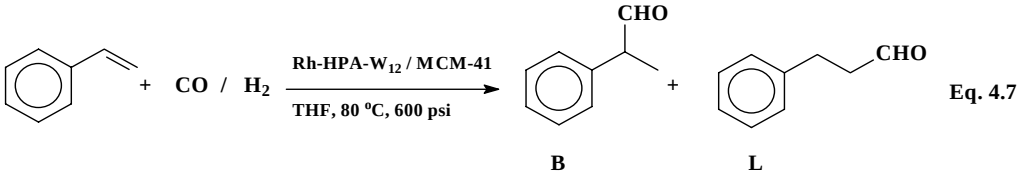
The possible role of water in the reaction was to allow the reduction of Rh (III) into rhodium (I) in the presence of carbon monoxide (Eq. 4.5). This effect was described by primet *et* a*l.* (131) and later by Davis *et* a*l.* (132) and it takes place at the surface of the silica as support:

$$Rh(III) + CO \longrightarrow Rh(III)—CO \xrightarrow{2CO + H_2O} Rh^{+}(I)(CO)_2 + CO_2 + 2H^{+} \quad \text{Eq. 4.5}$$

The idea of rhodium (III) carbonyl complex was formed on the surface of the MCM-41 is also supported, this rhodium (III) is reduced in the presence of water to rhodium (I) carbonyl intermediate. This later represents the most probable active catalytic species in the hydroformylation reaction of styrene. This reduction was produced on the surface and in the pores of the mesoporous materials. The use of high concentration of water inhibited the catalytic activity of the supported catalyst. It seems that the use of the excess of water enhances the conversion of $\mathbf{Rh(I)(CO)_2}$ into $\mathbf{Rh^0(CO)_m}$ and subsequently into rhodium cluter $\mathbf{Rh_6(CO)_{16}}$ ***via*** $\mathbf{Rh_4(CO)_{12}}$ (Eq. 4.6) as reported previously (132,133). These rhodium clusters are not active catalytic complexes under the present experimental conditions.

$$2\,Rh(I)(CO)_2 \xrightarrow{CO + H_2O} 2\,Rh^0(CO)_m \xrightarrow{CO/\text{ high } H_2O \text{ conc.}} Rh_4(CO)_{12} \xrightarrow{2\,Rh^0(CO)_m} Rh_6(CO)_{16} \quad \text{Eq. 4.6}$$

On the other hand, we have found that part of the rhodium catalyst was leaching



Eq. 4.7

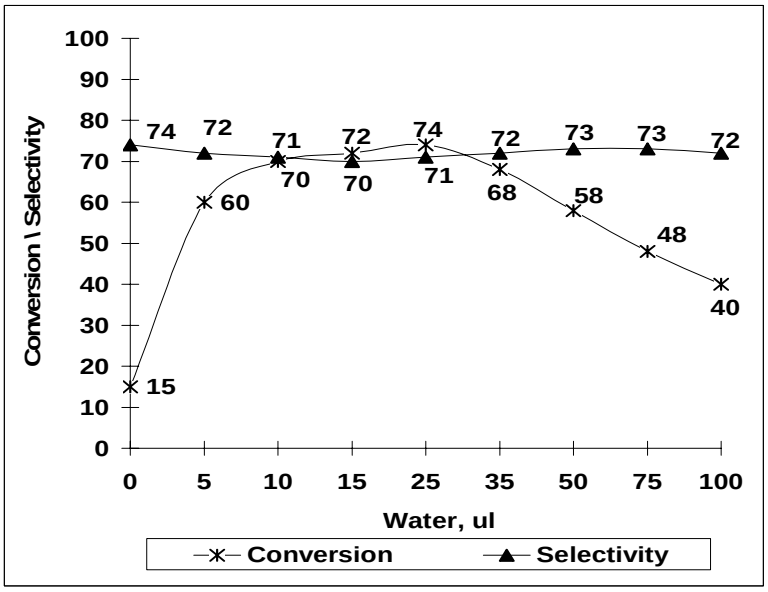


Figure 4.3. Hydroformylation of styrene. Effect of the volume of water (μl; 5μl = 0.278 mmol). Reaction conditions: **Rh*3*2W10MCM-*M*** (10 mg), styrene (0.5208 g= 5.0 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 80 ^oC, 6 h.

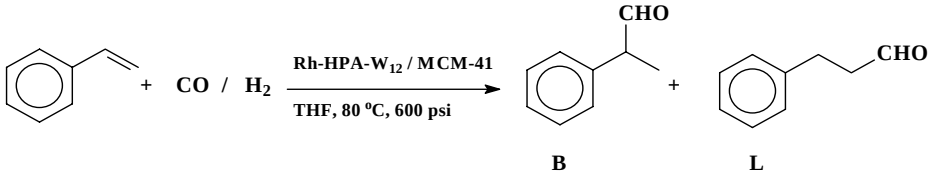
into the liquid phase at the end of the reaction, and the main catalytic hydroformylation might take place in the homogenous solution. In addition, we also believe that the reaction was also partially catalyzed by the heterogeneous system.

4.3.4 Hydroformylation of Styrene. Effect of the temperature with Rh(III) based catalyst

The effects of the temperature on the conversion and the selectivity of the hydroformylation of styrene have been studied with the catalyst **Rh*3***2**W**10**MCM**-*M* formed by the impregnation of $RhCl_3.3H_2O$ with HPA-W_{12} on MCM-41 in methanol (*M*) (Figure 4.4). The time of the reaction was fixed as 6 h. The results showed that the hydroformylation of styrene catalyzed by **Rh*3***2**W**10**MCM**-*M* (Figure 4.4) was relatively fast and there was no induction period observed. With **Rh*3***2**W**10**MCM**-*M* no reaction took place at 50 ^{o}C, and the conversion at 60 ^{o}C was 8 % with 90 % selectivity toward branched aldehyde. The conversion of the reaction increased and the selectivity of the branched aldehyde dropped with the increase of the temperature. At 100 ^{o}C and 120 ^{o}C the conversions were 94 % and 96 % but the selectivities in branched aldehyde decreased to 54 % and 47 % respectively. It is clear that the rate of the reaction and the selectivity are a function of temperature; the selectivity deteriorated at the end of the reaction.

4.3.5 Hydroformylation of Styrene. Effect of the type of solvent

The catalyst **Rh*3***2**W**10**MCM**-*M* in the hydroformylation of styrene showed higher catalytic activity mostly in polar oxygenated solvent having ether function such as tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and methyl tertiary butyl ether (MTBE) (Figure 4.4). The reactions were carried out at 80 ^{o}C for 6 h in the presence of 25



Eq. 4.8

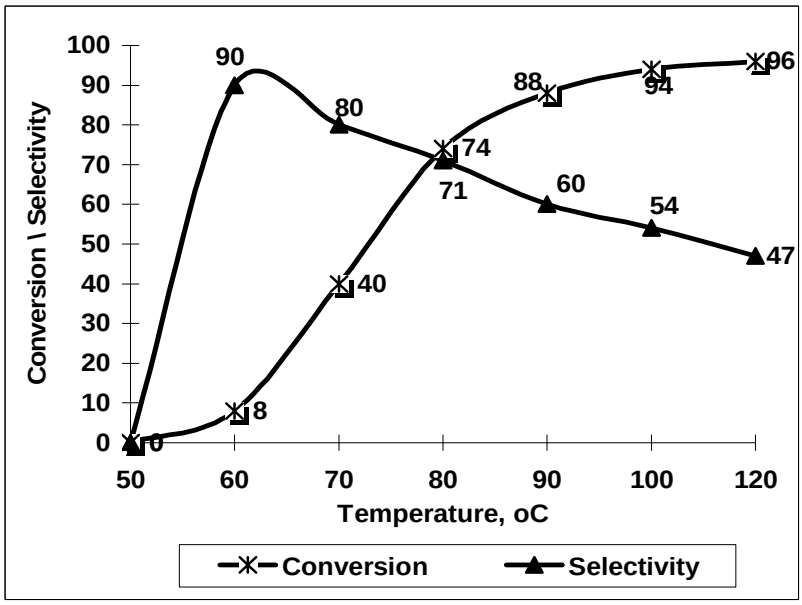
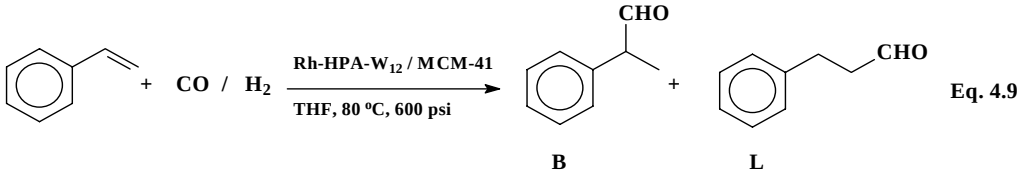


Figure 4.4. Hydroformylation of styrene. Effect of the Temperature. Reaction conditions: **Rh*3*2**W**10**MCM**-*M* (10 mg), styrene (0.5208g = 5.0 mmol), water (25 μl = 1.39 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 6 h.

μl of water. The significant conversions were obtained using THF, DME, and MTBE (74 %, 62 %, and 34 %, respectively). On the other hand, very low conversions of styrene (1-9 %) were detected with acetone, methyl ethyl ketone, hexane and 1,4-dioxane as a solvent, and no reaction was observed in dichloromethane (CH_2Cl_2), benzene, and toluene. Similar solvent effect has been also observed with the reaction catalyzed by the rhodium (I) **Rh^{A}*1*2W10MCM-*M*** (Figure 4.6). The same solvents have been considered for the reaction with **Rh^{A}*1*2W10MCM-*M***. Again, the highest conversion of styrene was obtained with THF followed by DME and MTBE as a solvent. Small or no conversions were obtained with the other considered solvents (1,4-dioxane, acetone, MEK, hexane, CH_2Cl_2, benzene, toluene). The effect of the type of solvent in figures 4.4 and 4.5 can be also explained in terms of dielectric constant. The two solvent that led to high conversions were THF and DME having dielectric constant of 7.52 and 7.20, respectively. The solvent of low (2.02-2.8) and high (9.08-20.70) dielectric constants gave very low conversion of styrene (2-28 %). It is very clear that the type of solvent has an enormous effect on the occurrence of the reaction. THF appeared to increase the catalytic activity and the stability of the key intermediate species [Rh(I)-HPA-W_{12}].

4.3.6 Hydroformylation of styrene derivatives by supported Rh(I) and Rh(III) catalysts

The reactions of the hydroformylation of styrene derivatives were carried out in the presence of the catalytic system **Rh^{A}*1*2W10MCM-*M***/CO/H_2 in THF as a solvent (Table 4.5, Eq. 11). Excellent conversions (95-99 %) were obtained in general after 16 h



Eq. 4.9

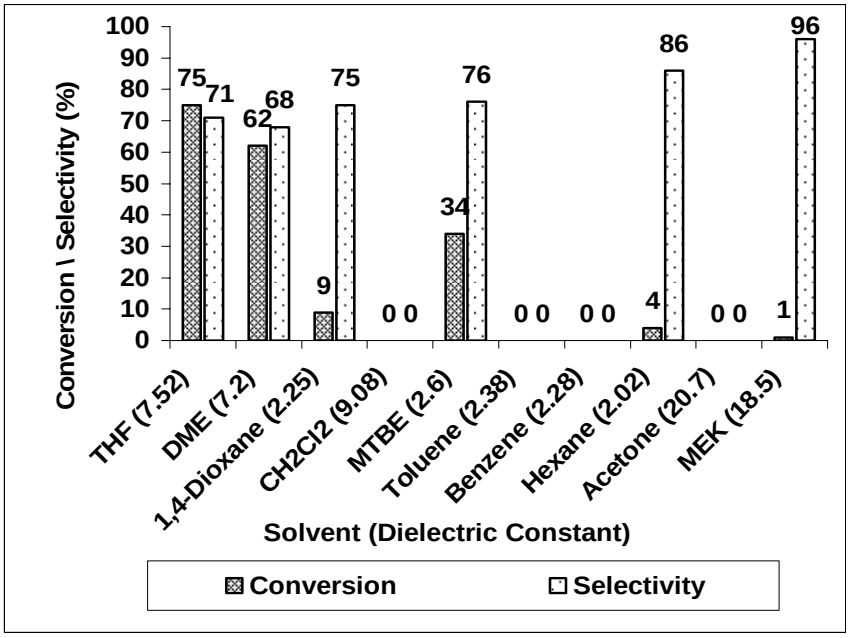
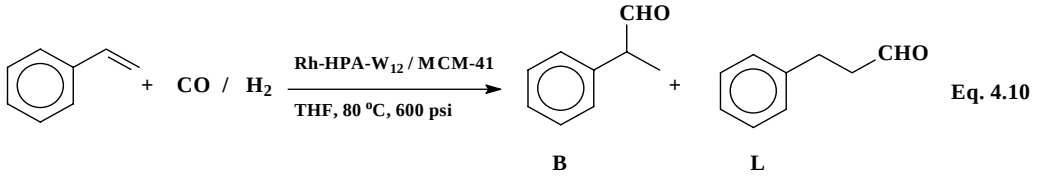


Figure 4.5. Hydroformylation of styrene by **Rh*3*2**W10**MCM**-*M*. Effect of the type of solvent. Reaction conditions: **Rh*3*2**W**10**MCM**-*M* (10 mg), styrene (0.5208g = 5.0 mmol), water (25 μl = 1.39 mmol), CO (300 psi), H_2 (300 psi), 80 ^oC, 6 h.



Eq. 4.10

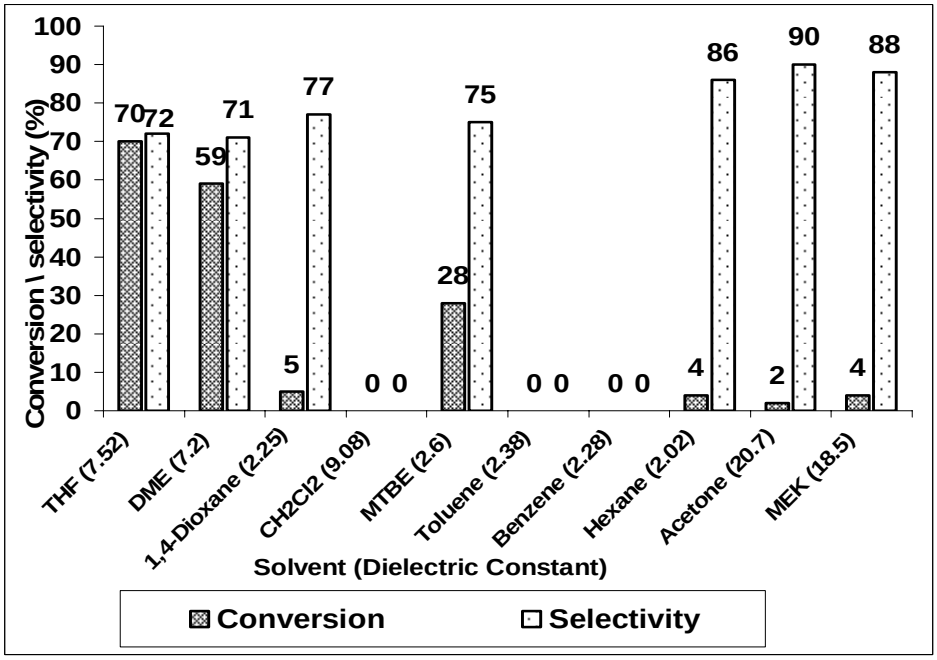


Figure 4.6. Hydroformylation of styrene by **Rh^{A}*1*2W10MCM-*M***. Effect of the type of solvent on the conversion and the selectivity. Reaction conditions: Catalyst **Rh^{A}*1*2W10MCM-*M*** (10 mg), styrene (0.5208 g = 5.0 mmol), CO (300 psi), H_2 (300 psi), 80 ^{o}C, 6 h.

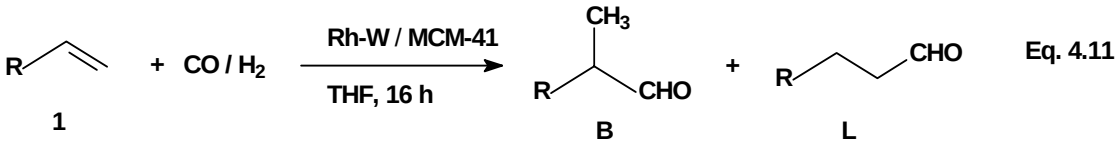
with mono-, di-, and trisubstituted benzene ring of the styrene with no major change in the selectivity in the corresponding branched aldehyde (69-72%) (Table 4.5, entries 1-12). The styrene derivatives with electron withdrawing groups (chloro, or nitro) in ortho, para, or meta position, were also very reactive in the hydroformylation reaction. The conversions were very high 88-96% with the selectivities maintained again at the same level (68-73 %) (Table 4.5, entries 13-18). Interestingly, 2-vinylnaphthalene was almost totally converted (99 %) with higher selectivity (79 %) toward the branched aldehyde (**B)**. It is important to mention that no hydrogenated by-products were detected with all substrates.

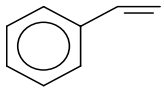
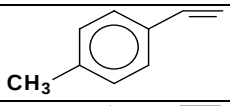
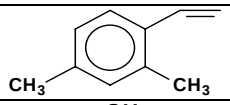
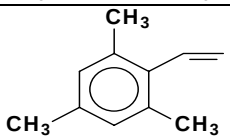
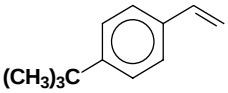
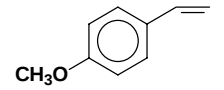
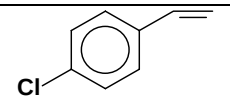
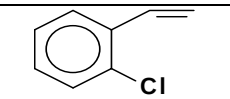
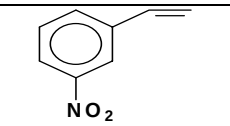
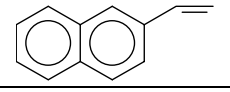
4.3.7 Effect of the rhodium leaching on the hydroformylation of styrene

The results of the hydroformylation of styrene by supported showed that the amount of leaching of rhodium from the catalyst system **Rh*3***2**W**10**MCM**-*M* increased with the addition of water and also with the increase of the temperature. The leaching of rhodium was significant with the rhodium (I) catalyst **Rh^{A}*1***2**W**10**MCM**-*M* even at 80 ^{o}C for 16 h or at 100 ^{o}C for 6 h. On the other hand, we have performed some tests on the effects of the leaching materials on the catalytic reaction. **Rh*3***2**W**10**MCM**-*M* was treated with CO / H_2 at 80 ^{o}C for 16 h in THF as a solvent and in the absence of styrene. After the reaction, the liquid and solid phases (LP and SP) were separated. The liquid phase (LP) contains the leached out materials, and the solid phase (SP) was mainly formed of MCM-41 supported with the non-leached out catalyst. We have considered both phases in the hydroformylation reactions. To the LP, 5.0 mmol of styrene and 25 µl of water were added and the reaction was run for 16 h, under 600 psi of CO / H_2. The reaction products

Table 4.5. Hydroformylation of various aryl alkenes by

Rh^{A}*1*2W10MCM-*M* or Rh*3*2W10MCM-*M* with CO/H_2 in THF.[a]



No	Substrate 1	Catalyst	Conversion[b] %	Product Distribution[c] % B / L
1		Rh (I)	97	69 / 31
2		Rh(III)	98	69 / 31
3		Rh (I)	94	74 / 26
4		Rh(III)	99	72 / 28
5		Rh (I)	95	73 / 27
6		Rh(III)	95	70 / 30
7		Rh (I)	95	75 / 25
8		Rh(III)	95	72 / 28
9		Rh (I)	97	74 / 26
10		Rh(III)	97	70 / 30
11		Rh (I)	95	70 / 30
12		Rh(III)	95	71 / 29
13		Rh (I)	98	71 / 29
14		Rh(III)	96	73 / 27
15		Rh (I)	92	70 / 30
16		Rh(III)	96	73 / 27
17		Rh (I)	88	69 / 31
18		Rh(III)	64	68 / 32
19		Rh (I)	98	72 / 28
20		Rh(III)	64	68 / 32

a) Reaction conditions: catalyst (10 mg), styrene (5.0 mmol), (THF (5 ml), 600 psi ($CO / H_2 = 1/1$), 80 ^{o}C, 16 h.
Catalyst: **Rh^{A}*1*2W10MCM-*M*** [Rh (I)] or **Rh*3*2W10MCM-*M*** [Rh (III)].

b) Determined by GC.

c) Determined by GC and ^{1}H NMR.

were analyzed after the reaction and gave a conversion of 49 % of styrene into aldehydes. (B / L = 72 / 28). Traces of products were detected with the reaction involving the SP under the same conditions. The same catalyst **Rh*3*2W**10**MCM**-*M* was treated with carbon monoxide only (600 psi) for 16 h in THF. The subsequent LP was also considered in the hydroformylation of styrene under the conditions given above leading to a conversion of 33 % (B / L = 75 / 25). The liquid phase of the catalyst **Rh*3*2W**10**MCM**-*M* treated with H_2 only (600 psi) in THF gave no reaction in the hydroformylation of styrene. However, the solid phase gave 4 % of conversion of styrene after 16 h of reaction.

Similarly, **Rh^{A}*1*2W**10**MCM**-*M* was treated with CO / H_2 (600 psi) for 16 h in THF as a solvent. The liquid phase was used in the presence of styrene (5.0 mmol) at 80 ^{o}C for 16 h. The conversion was 26 % (B/L = 76 / 24) and no reaction was observed with the solid phase in the catalytic test. Based on these important results, it is extremely difficult to confirm that the hydroformylation of styrene took place mainly by the homogeneous system *via* the leaching out of the active catalyst in the solution. There is a clear role of the heterogeneous catalytic system in the reaction with both Rh (I) and Rh (III) based catalysts. The preliminary percentage of leaching may not be very accurate due the small amount of the supported catalyst (10 mg) used in the reaction.

In an effort to characterize possible active intermediates that leached out the surface of the catalysts, we have carried out a FTIR study on the catalysts **Rh^{A}*1*2W**10**MCM**-*M* and compared to **Rh*3*2W**10**MCM**-*M*. The set of FT-IR spectra are given in Appendix Figure A4.7a & b. First, we have recorded the FTIR spectra of the pure commercial complexes **[Rh(COD)Cl]$_2$** (Figure A4.7a) and **$H_3PW_{12}O_{40}$ (HPA-W_{12})** (Figure A4.7b). A reddish complex has been isolated from the reaction of **[Rh(COD)Cl]$_2$** and **$H_3PW_{12}O_{40}$** in methanol at room temperature (25 ^{o}C) for 20 h. The FTIR spectrum

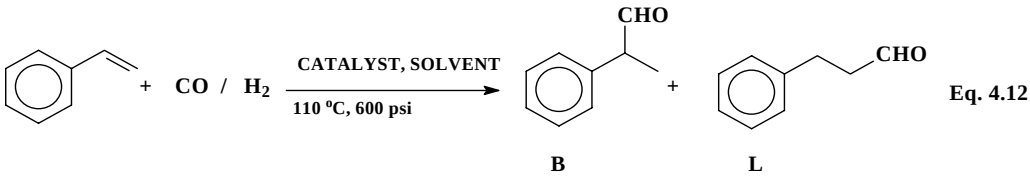
(Figure A4.8a) of the later complex showed a significant change in the structure of **[Rh(COD)Cl]$_2$** but not in the structure of **HPA-W$_{12}$** (802, 892, 980, and 1080 cm^{-1}). Two new absorption bands 1628 and 1706 cm^{-1}, appeared after the reaction, and could be attributed to a complex **Rh-HPA-W$_{12}$** (Appendix Figure 4.8b). In another experiment, **[Rh(COD)Cl]$_2$** and **H$_3$PW$_{12}$O$_{40}$** were treated with a syngas (600 psi, CO / H_2 = 1/1) in THF at 80 ^oC for 16 h in the absence of styrene. At the end of the reaction the solvent was quickly evaporated under vacuum and the solid material obtained was analyzed by FTIR. The infrared spectrum of the product (Figure A4.8c) showed new absorption bands (1726-1780 cm^{-1}), which can be attributed to **Rh-CO-Rh** bridging **C-O** stretching (135). Another two or three bands appeared between 2000-2072 cm^{-1} which correspond probably to absorption of terminal carbonyl groups of **Rh(CO)$_2^+$** (136,137). To our knowledge, the band appearing at 2240 cm^{-1} has not been reported in the literature for the rhodium carbonylation chemistry. This band could be attributed to a complex formed between **[Rh(COD)Cl]$_2$** and **H$_3$PW$_{12}$O$_{40}$** under the hydroformylation conditions probably through **W-O….Rh** interaction. This interaction would probably strengthen the terminal **CO** bond, and therefore, inducing a shift toward higher wave numbers. The other important experiment was realized with **Rh^A*1*2MCM-*M***, obtained by the impregnation of **[Rh(COD)Cl]$_2$** on MCM-41 in methanol as a solvent in the absence of the heteropolyacid **H$_3$PW$_{12}$O$_{40}$**. **Rh^A*1*2MCM-*M*** was also treated with syngas (600 psi, CO / H_2=1/1) at 80 ^oC for 16 h in THF as a solvent. The liquid phase (LP) was separated from the solid phase (SP) by centrifuging. The solvent (THF) in the LP was evaporated under vacuum giving bright red solid materials. This later solid material was analyzed by FTIR giving a spectrum (Figure A4.8d) with significant bands at 1728 and 2068 cm^{-1} and small band at around 1780 cm^{-1}. These were previously attributed to bridging carbonyl of **Rh-CO-Rh**

and also to terminal carbonyl groups of **$Rh(CO)_2^+$**. No band appeared at 2240 cm^{-1}. Similarly, the catalyst **Rh^A*1*2W10MCM-*M*** was also treated under the hydroformylation conditions. The liquid phase, separated from the solid phase, was evaporated under vacuum to give a reddish solid material. This later solid material gave an infrared spectrum (Figure A4.8e) comparable to the spectrum obtained from the complex formed with **$[Rh(COD)Cl]_2$** and **$H_3PW_{12}O_{40}$**. Strong absorption bands were observed at 1724 and 1772 cm^{-1} attributed to probable formation of **Rh-CO-Rh**. Bands of small absorption were also observed at approximately 2000-2080 cm^{-1} and 2360 cm^{-1}, which were attributed to terminal carbonyl groups of **$Rh(CO)_2^+$** and **$[Rh(CO)_x$-$PW_y]$**, respectively.

The strong and sharp bands at 1724, 1772, and 2250 cm^{-1} were also observed from the solid material obtained from the liquid phase after the treatment of catalysts **Rh*3*2W10MCM-*M*** under the hydroformylation conditions. It is important to recall that the catalyst **Rh*3*2W10MCM-*M*** was obtained from **$RhCl_3.\ 3H_2O$** and **HPA-W_{12}** impregnated on MCM-41 in methanol as a solvent. The analysis of the FTIR spectra made clear the role of the heteropolyacid in the formation of an active complex in solution and most probably on surface. These active species are not yet characterized and a separate study is needed to isolate, analyze and characterize the active intermediates. Subsequently, more experiments and a detailed study must be considered in a separate project to explore in detail the identification of the rhodium-heteropolyacid impregnated systems by in situ FT-IR. Other important tests with rhodium impregnated in ethanol were also performed. The study of rhodium leaching out from the surface of the MCM-41 and the effect of the leached-out material on the hydroformylation of styrene has also been considered with the following catalysts:

1. **Rh*15*MCM-E**

Table 4.6. Study effect of the catalytic activity of the leached material on the hydroformylation of styrene.[a]



Eq. 4.12

Entry	Catalyst	Cycle	Time h	Conversion[b] %	Product Distrubution[c]	
					B %	L %
1	**Rh*15*MCM-*E* SP**	1	16	93	55	45
2		2	16	10	55	45
3	**Rh*15*MCM-*E* LP**	1	16	84	62	38
4		2	5	64	58	42
5	**Rh*15*Mo*10*MCM-*E* SP**	1	4	37	63	37
6		2	6	84	63	37
7		3	9	98	59	41
8	**Rh*15*Mo*10*MCM-*E* LP**	1	4	5	63	37
9	**Rh*35*Mo*10*MCM-*E* SP**	1	16	40	57	43
10		2	16	11	57	43
11	**Rh*35Mo10MCM-E* LP**	1	16	80	59	41
12		2	16	52	64	36

a) Reaction conditions: catalyst (50 mg), styrene (5.0 mmol), cyclohexane (5 ml), 600 psi ($CO / H_2 = 1/1$), 110 °C.
b) Determined by GC.
c) Determined by GC and ^1H NMR.

2. **Rh***15*Mo*10*MCM-E

3. **Rh***35*Mo*10*MCM-E

The catalysts were treated at 600 psi of CO / H_2 (1:1), 5.0 ml of cyclohexane in the absence of styrene at 110 ^oC for the required number of hours. After the reaction, the liquid and solid phases (LP and SP) were separated by centrifuging followed by filtration. The liquid and solid were used in the subsequent recycling experiments. The results, as shown in Table 4.6, clearly indicate the effectiveness of heteropolyacid as tethered agent.

4.3.8 Recycling of the supported catalysts in the hydroformylation of styrene

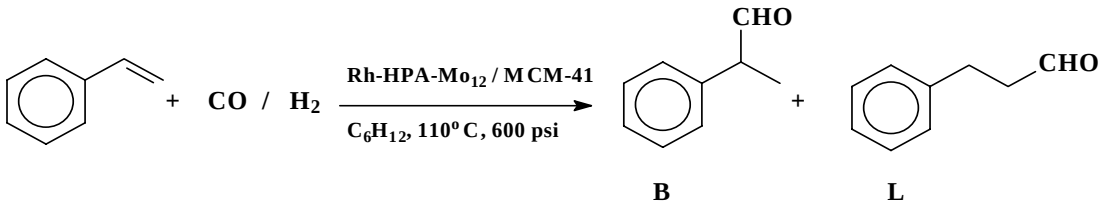
Various heterogeneous catalysts were synthesized and tested in successive hydroformylation reactions of styrene to investigate the effect of the support and anchoring agents on the recycling ability of the catalysts.

Hydroformylation of styrene proceeded in the presence of the catalytic amount of **Rh***15*Mo*10*MCM-*E* affording a good yield and selectivity for the branched and linear aldehydes, even in the absence of free PPh_3 or any other ligand often used in homogeneous or immobilized systems (133). The results are presented in Figure 4.7. The conversions of over 95 % were achieved in 3 h for 5 cycles with branched to linear ratio remaining fairly constant (~55/45), while cycles 6 and 7 required a little more time (9 h and 12 h, respectively) for the same conversion, while the selectivity remain the same. It is very clear that the catalyst system is not leached out in the first cycle, and hence can be recycled at least 7 times.

To investigate the role of heteropolyacid as tethered agent, **Rh***15*MCM-E was prepared by refluxing the same 5% of $HRhCO(PPh_3)_3$, and MCM-41 in dry ethanol, but without heteropolyacid. The catalyst was tested under the same above reaction conditions

with **Rh***15*MCM-*E* and the results are shown on Figure 4.8. The conversion was again very high (> 95 %) and was achieved in 3 h for the first 3 cycles, but for the cycles 4 and 5, the reaction has to be run for 12 h and 20 h to achieve similar conversion. A clear indication of faster leaching out of this catalyst could be seen in the fifth cycle, where less than 40 % conversion was achieved after 20 h of reaction. The catalyst was almost deactivated after the fifth cycle. The branched to linear ratio was almost the same as in the previous experiment.

These results indicate clearly the effect of the heteropolyacid in the formation of stable and active supported catalysts. The catalysts prepared by impregnation rhodium complex $\mathbf{Rh^A}$ with different heteropolyacids of Keggin structure such as $H_3PW_{12}O_{40}$ (Figure 4.9) and $H_4SiMo_{12}O_{40}$ (Figure 4.10) were studied. The catalyst that incorporates phosphotungstic acid, $H_3PW_{12}O_{40}$, was found to be as active as the catalyst made of $H_3PMo_{12}O_{40}$. The supported catalyst **Rh***15W10*MCM-*E* was still very active even after running the catalyst for seven cycles. Earlier reports have shown that phosphotungstic acid to be very effective tethering agent in hydroformylation (65,131) and hydrogenation of functionalized and unfunctionalized alkene, alkynes and aldehydes (61). *Si* was used as central atom in place of P in HPA-W_{12} to produce the supported catalyst **Rh***15***SiW**10**MCM**-*E*. Surprisingly, the use of *Si* reduced the recycling ability of the catalyst even when the reaction is ran at 110 ^{o}C. Cycle 4 gave less than 60 % even after running the experiment for 40 h, but the branched-linear ratios (61 / 39) were slightly higher than for **Rh***15***Mo**10**MCM**-*E* (55 / 45) ran under the same conditions (110 ^{o}C) (Figure 4.10). The lower recycling potential of the **Rh***15***SiW**10**MCM**-*E* is probably related to the Si-O-Si interaction between HPA and MCM-41 or the possible decomposition of



Eq. 4.13

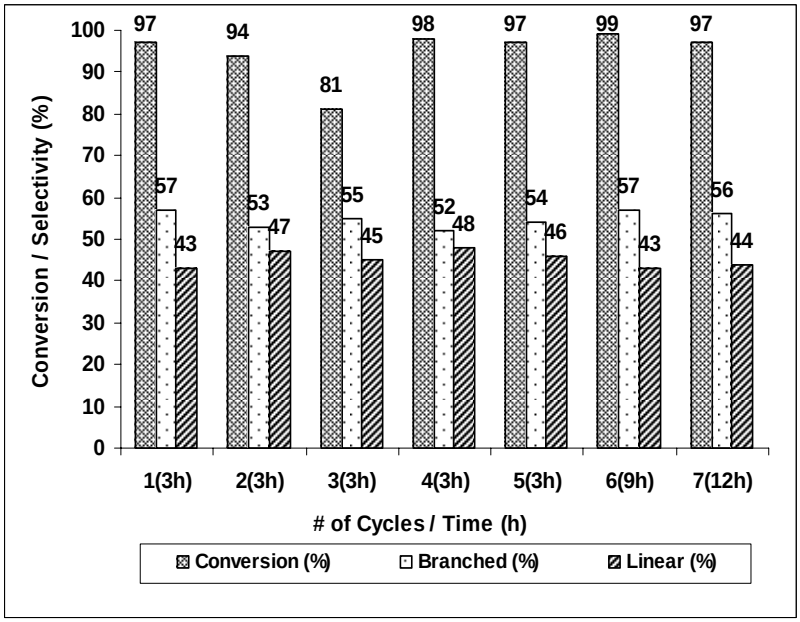
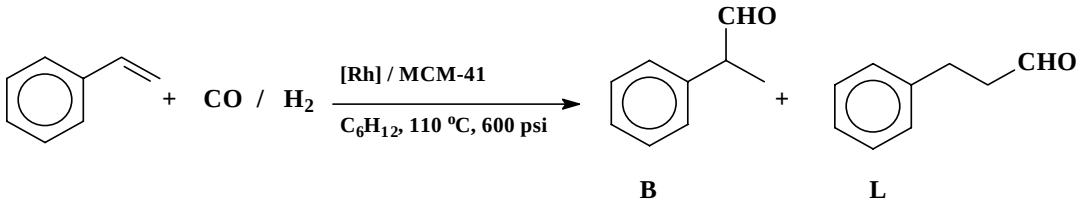


Figure 4.7. Hydroformylation of styrene. The recycling of the catalyst **Rh*15*Mo10MCM-*E***. Reaction conditions: **Rh*15*Mo10MCM-*E*** (50 mg), styrene (0.5208 g = 5.0 mmol), cyclohexane (5.0 ml), CO (300 psi), H_2 (300 psi), 110 ^{o}C.



Eq. 4.14

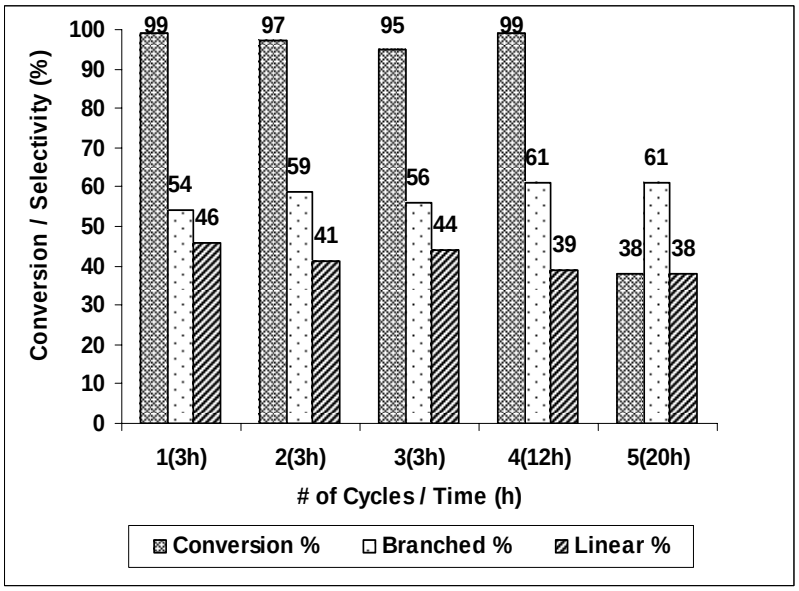
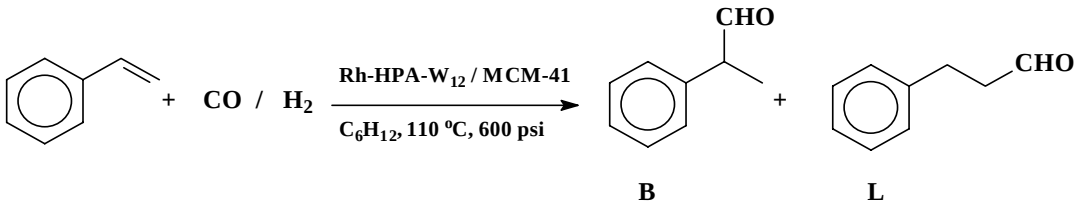


Figure 4.8. Hydroformylation of styrene. The recycling of the catalyst **Rh*15*MCM-*E***. Reaction conditions: **Rh*15*MCM-*E*** (50 mg), styrene (0.5208 g = 5.0 mmol), cyclohexane (5.0 ml), 110 ^{o}C, CO (300 psi), H_2 (300 psi).



Eq. 4.15

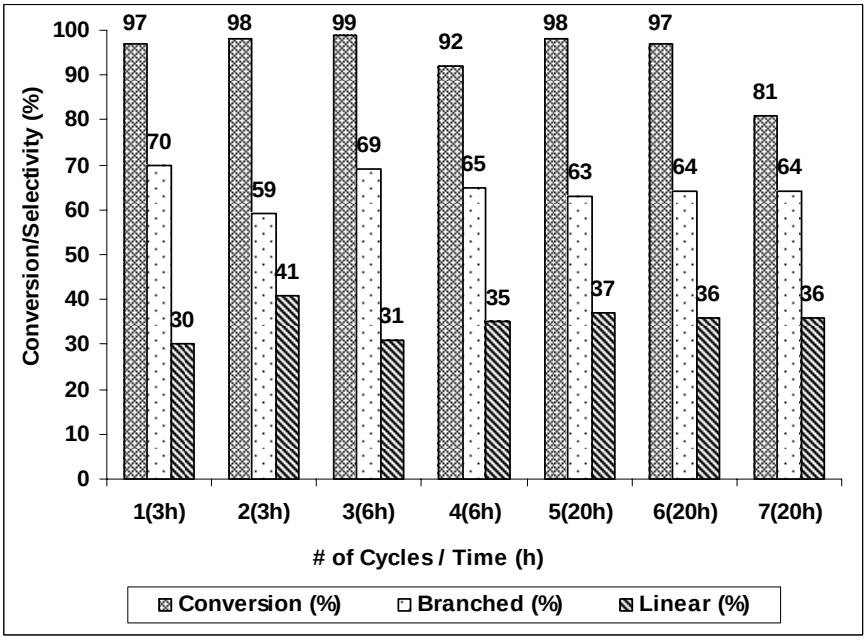
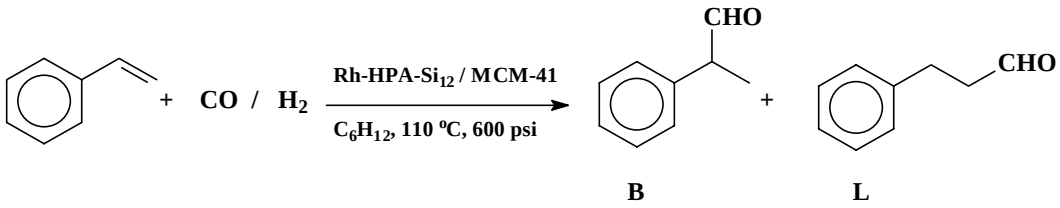


Figure 4.9. Hydroformylation of styrene.The recycling of the catalyst **Rh***15W10*MCM-E. Reaction conditions: **Rh***15W10*MCM-E (50 mg), styrene (0.5208 g = 5.0 mmol), cyclohexane (5.0 ml), 110 ^{o}C, CO (300 psi), H_2 (300 psi).



Eq. 4.15

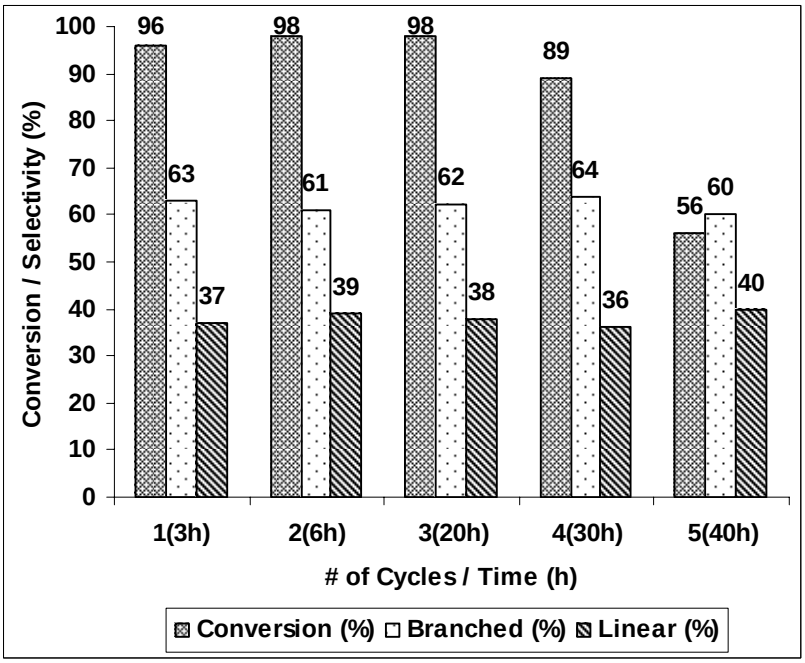
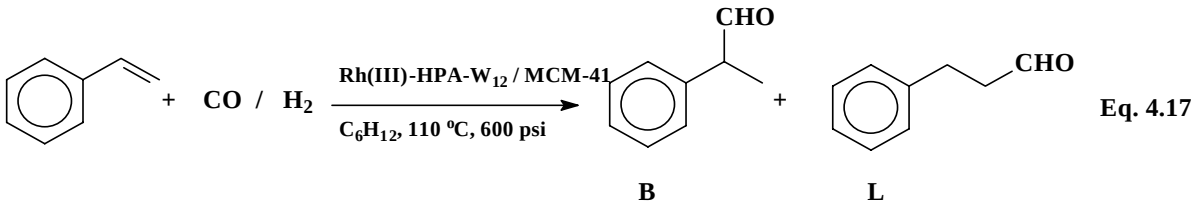


Figure 4.10. Hydroformylation of styrene. The recycling of the catalyst **Rh***15***SiW**10**MCM**-*E*. Reaction conditions: **Rh***15***SiW**10**MCM**-*E* (50 mg), styrene (0.5208 g = 5.0 mmol), cyclohexane (5.0 ml), 110 ^{o}C, CO (300 psi), H_2 (300 psi).



Eq. 4.17

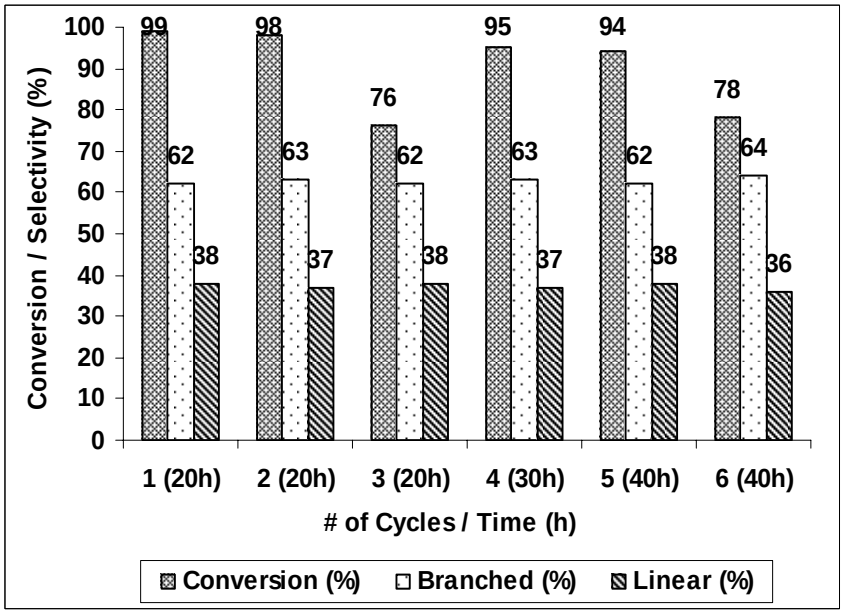


Figure 4.11. Hydroformylation of styrene. The recycling of the catalyst **Rh***35***W**10MCM-E. Reaction conditions: **Rh***35W10MCM*-E (50 mg), styrene (0.5208 g = 5.0 mmol), cyclohexane (5.0 ml), 110 ^{o}C, CO (300 psi), H_2 (300 psi).

HPA-W_{12} on the surface of the catalyst subsequently lowering the catalytic activity of the catalyst. We believe that the HPA–MCM-41 interaction goes through W-Si bond formation, which probably affects the recycling ability of the catalyst. The reaction of hydroformylation of styrene was also studied using the supported system obtained from Rh(III)-HPA-W_{12}-MCM-41 (Figure 4.11). It is important to note again that 5 % (27.1 mg) of $RhCl_3.3H_2O$ were refluxed with 500 mg MCM-41 already functionalized with 10 % (56.8 mg) of $H_3PW_{12}O_{40}$.

The activity of the catalysts based on Rh (III), as expected, is generally lower than Rh (I) based catalyst. For example, cycle 1 with **Rh**35**W**10**MCM**-*E* gave 99 % conversion with 61 / 39 branched to linear ratio after 20 h reaction time compared to 3 h in the case of **Rh***1*5**W**10**MCM**-*E*. In the same way cycles 2, 3, 4, 5 and 6 was ran for 20, 20, 30, 40 and 40h respectively to obtained a significant amount of yield compared to 4, 6, 6, 20 and 20 h respectively for **Rh***1*5**W**10**MCM**-*E* catalyst (Figure 4.9).

4.4 Conclusion

The study of the hydroformylation of styrene and its derivatives by the heterogeneous catalysts led to interesting results. The impregnated catalysts based on rhodium (III) showed high catalytic activity in the presence of water. **Rh***3*2**W**10**MCM**-*M* was among the catalysts that gave the highest conversion at 80 ^{o}C. The amount of water added should be controlled because the use of excess of water did inhibit the reaction. The supported catalysts based on rhodium (I) were also very active and produce high conversions of styrene and styrene derivatives. The detailed study of the heterogeneous catalyst recycling showed clearly the role of the heteropolyacid in the supported catalyst. It is important to note that the influence of the heteropolyacid was in both catalyst systems

that involve rhodium (I) and rhodium (III). The choice of the solvent of impregnation was very important in order to minimize the leaching. Cyclohexane as a solvent does not enhance the leaching of Rh(III) and Rhodium (I) supported catalysts. **Rh^{A}*1*5W10MCM-*E*** catalyzed efficiently the hydroformylation of styrene with excellent conversion. It was very clear that the presence of HPA-W_{12} or HPA-Mo_{12} with Rh(I) or Rh(III) on the support increased the catalytic activity of rhodium catalysts by improving the conversions of styrene and the recycling of the supported catalyst.

CHAPTER 5

5.0 SUPPORTED RHODIUM CATALYZED HYDROFORMYLATION OF ALKYL ALKENES

5.1 Introduction

As a result of the high value of long chain oxygenates as fine chemicals, hydroformylation of alkyl alkenes have extensively been investigated in both homogeneous and heterogeneous catalysis (10,138,139). Thus far, the preparation of heterogeneous hydroformylation catalysts has made use of various supports, such as organic polymers, SiO_2, Al_2O_3, MgO, ZnO, clays, active carbons and zeolites (3,6,128,140). Although zeolites provide an excellent catalyst support with high surface area and unusual catalytic properties, their applications in catalysis are limited by their relatively small pore openings.

The synthesis of the first mesoporous molecular sieve MCM-41 by Mobil's researchers in 1991–1992 opened up the opportunities to apply ordered mesoporous materials to the areas of catalysis, separation, sensors and opto-electric devices (141). Apart from its high surface area (>700 m^2/g), MCM-41 possesses a hexagonal arrangement of highly uniform sized mesopores (15–100 Å) that shows minimal pore size variation. The larger pore sizes of MCM-41 facilitate the flow of reactant and product molecules in and out of the pore system, making them ideal for shape-selective conversions of bulky molecules encountered in the upgrading of heavy residues in refineries and the manufacture of fine chemicals. Within a short period of time, a large

number of studies have been made concerning the potential application of MCM-41 in catalysis.

Functionalization of MCM-41 with 3-aminopropyltrimethoxylsiline (APTS), and subsequent encapsulation and anchoring of $HRh(CO)(PPh_3)_3$ in the mesoporous material was reported (51). Other studies have been reported concerning hydroformylation catalysts prepared by linkage of rhodium complexes, such as $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$ to MCM-41 phosphines, amines and thiols (62,64). The effects of the three donor ligands on the catalytic properties in 1-hexene hydroformylation were briefly evaluated and compared. Novel approach to hetorogenizing Wilkinson's hydroformylation catalyst, $HRh(CO)(PPh_3)_3$, by tethering it to Zeolite-Y through heteropolyacid has been reported (65).

This chapter consists of the results of supported rhodium catalyzed hydroformylation of alkyl alkenes. The highly active, stable and reusable catalyst composed of $HRh(CO)(PPh_3)_3$ tethered to MCM-41 through heteropolyacid.

5.2. Experimental

5.2.1 General

All chemicals, otherwise stated, including solvents and alkenes were highly pure (>99%) and were purchased from Sigma-Aldrich Company. The solvents used in the experiments, such as THF, hexane, cyclohexane, CH_2Cl_2, benzene, 1,4-dioxane, methyl ethyl ketone (MEK), acetone, 1,2-dimethoxyethane (DME), methanol, ethanol, and others were HPLC grade and were stored under nitrogen over activated 3Å molecular sieves. Anisole, tetraethoxysilane (TEOS), n-hexadecyltrimethyl ammonium (or cetyltrimethyl

ammonium) bromide, ammonium hydroxide, tetramethyl ammonium bromide (25% by weight solution in water), triphenylphosphite [$P(OPh)_3$] and $H_3PW_{12}O_{40}$. $25H_2O$ were used without any further purification. The rhodium complexes $RhCl_3.3H_2O$, $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, and $RhHCO(PPh_3)_3$ (Strem Company) were used without purification.

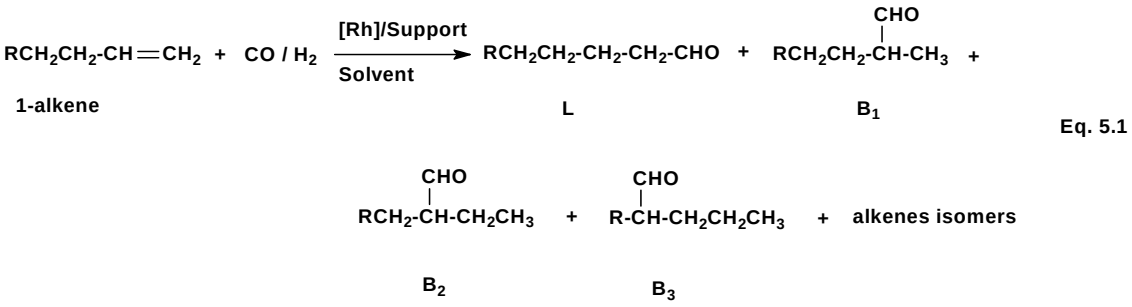
5.2.2 General procedure for the Heterogeneous hydroformylation

The following general procedure was considered for 1-octene adopted as model substrates for alkyl alkenes in the hydroformylation reaction. 50 mg or 20 mg of the supported catalyst was weigh into a glass liner equipped with magnetic bar. 5.0 ml of dry solvent was added to the liner. 5.0 mmol (= 0.5608 g) of 1-octene was added, and the liner placed into 25 ml high-pressure Parr autoclave. The autoclave was flushed thoroughly three times with carbon monoxide, subsequently pressurized with 300 psi of CO and 300 psi of hydrogen. The autoclaves were heated on hotplates controlled by temperature sensor to maintain the temperature constant (± 0.5 ^oC). The rate of stirring was maintained at 750 rpm. After the reaction time elapses, the autoclave was cooled to room temperature and the gas carefully released under fume hood. The reaction mixture was centrifuged twice to separate the solid catalyst from the liquid products. The solid catalyst was dried in oven at 60 ^oC and used again in another catalytic cycle. 100 µg of n-decane were added to mixture as internal standard to determine the conversion of 1-octene. The products were identified using GC, GC-MS, ^1H NMR and ^{13}C NMR techniques. The ratio of the branched **(B_1), (B_2), (B_3),** and linear aldehydes **(L**) were determined by GC and ^1H NMR.

5.3 Results and discussion

5.3.1 Hydroformylation of 1-octene by Rh-HPW_{12}-MCM-41 system. Effect of the type of the supported catalyst

The hydroformylation of 1-octene was examined by Rh(I) and Rh(III) supported catalysts, prepared by the impregnation of $Rh^{III}Cl_3.3H_2O$, $HRh^{I}CO(PPh_3)_3$ or $[Rh^{I}(COD)Cl]_2$ with HPW_{12} on MCM-41 in methanol (*M*) or ethanol (*E*) as a solvent (Eq. 5.1, Table 5.1).



The results obtained with 1-octene, considered as a model substrate, showed clearly the higher catalytic activity of the supported catalysts that incorporate both rhodium (III) complex and HPW_{12}. The conversion obtained with the catalyst **Rh*3***2**MCM**-*M*, containing no heteropolyacid, was 64 % compared to 94 % with **Rh*3***2**W**10**MCM**-*M* (Table 5.1, entries 1-2). The same trends were observed with the catalysts **Rh*3***5**MCM**-*E* and **Rh*3***5**W**10**MCM**-*E* obtained by the impregnation in ethanol as a solvent (Table 5.1, entries 3-4). It has been shown in the previous chapter (Chapter 4, section 4.3.3) that hydroformylation of styrene can be enhanced by the addition of water to the system catalyzed by **Rh*3***2**W**10**MCM**-*M*. With 1-octene, when water (25 µl) was added to the liquid phase along with **Rh*3***2**W**10**MCM**-*M*, the reaction was seriously inhibited and the conversion of 1-octene dropped from 94 % to 26 % after 16 h. Furthermore, the addition of monophosphine (PPh_3), or diphosphine (dppb) ligand to

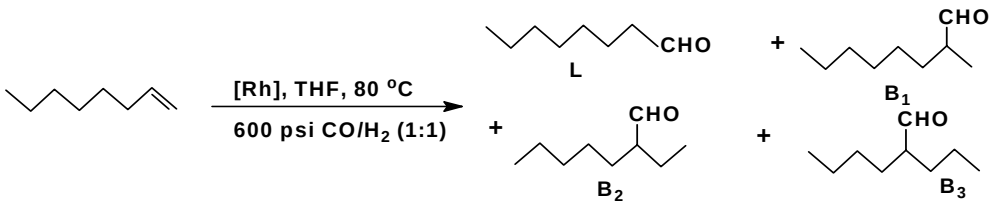
Rh*3*2W10MCM-*M* totally inhibited the reaction while monophosphite ligands contributed to the serious decrease of the conversion of the reaction. For example, when triphenylphosphite $P(OPh)_3$ was used, the conversion of 1-octene dropped from 94 % to 35 % (Table 5.1, entry 5).

The presence of water may enhance the conversion of **$Rh(I)(CO)_2$** into **$Rh^0(CO)_m$** and subsequently into rhodium cluster **$Rh_6(CO)_{16}$** ***via*** **$Rh_4(CO)_{12}$** (132,133). PPh_3 may lead to stable and inactive rhodium-phosphine or diphosphine intermediates (1).

Higher catalytic activity of rhodium (I) supported catalysts was observed compared to rhodium (III) catalysts in terms of conversion at the same experimental conditions (Table 5.1, entries 6-15). The rhodium (I) based supported catalysts, prepared by impregnating Rh (I) with or without HPW_{12} on MCM-41, were also used in the hydroformylation of 1-octene. The conversion of 1-octene obtained with the catalysts **Rh^A*1*2W10MCM-*M*,** **Rh^A*1*2W10MCM-*E*,** **Rh^B*1*2W10MCM-*M*,** and **Rh^B*1*2W10MCM-*E*** were excellent (94-96 %) and higher than the conversions obtained with their counterparts lacking HPW_{12}, namely **Rh^A*1*2MCM-*M*,** **Rh^A*1*2MCM-*E*,** **Rh^B*1*2MCM-*M*,** and **Rh^B*1*2MCM-*E***. These results showed once again the advantages of the use of the heteropolyacid HPW_{12} on the catalytic activity of these systems in the hydroformylation of 1-octene. However, **Rh^B*1*5W10MCM-*E*** with 5 % rhodium gave excellent conversion of 1-octene and similar selectivity in aldehydes (Table 5.1, entry 15).

The optimization of the reaction conditions required the study of the effects of the type of catalyst, the temperature, the reaction time, and the type of solvent.

Table 5.1 Rhodium supported catalysts in the heterogeneous hydroformylation of 1-octene.[a]



Eq. 5.2

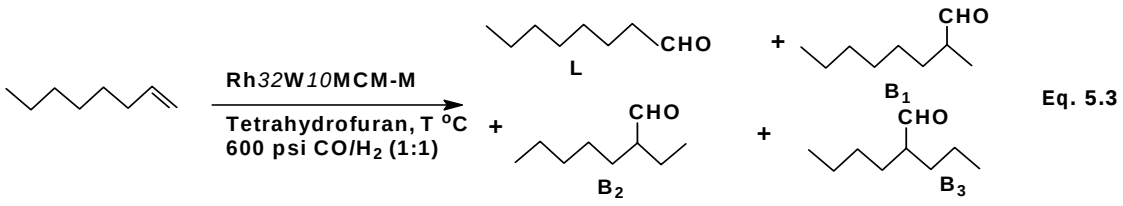
Entry	Catalyst	Conversion[b] %	Product Distribution[c] % B_1 / B_2 / B_3 / L	Octenes[b] %	
				1-Octene	Other Octene Isomers
1	**Rh*3*2MCM-*M***	64	35 / 1 / 0 / 64	90	10
2	**Rh*3*2W10MCM-*M***	94	37 / 5 / 8 / 50	17	83
3	**Rh*3*5MCM-*E***	66	26 / 0 / 0 / 74	55	45
4	**Rh*3*5W10MCM-*E***	88	33 / 1 / 0 / 66	87	13
5[d]	**Rh*3*2W10MCM-*M***	35	31 / 2 / 3 / 64	22	78
6	**Rh^A*1*2MCM-*M***	77	35 / 2 / 4 / 59	10	90
7	**Rh^A*1*2W10MCM-*M***	96	37 / 3 / 6 / 54	11	89
8	**Rh^A*1*2MCM-*E***	75	34 / 3 / 4 / 58	13	87
9	**Rh^A*1*2W10MCM-*E***	95	38 / 2 / 5 / 55	9	91
10	**Rh^B*1*2MCM-*M***	79	36 / 3 / 4 / 57	8	92
11	**Rh^B*1*2W10MCM-*M***	96	34 / 8 / 3 / 55	5	95
12	**Rh^B*1*5MCM-*E***	92	35 / 10 / 4 / 51	8	92
13	**Rh^B*1*5W10MCM-*E***	94	33 / 9 / 4 / 54	7	93
14[e]	**Rh^B*1*5MCM-*E***	80	37 / 10 / 6 / 47	10	90
15[e]	**Rh^B*1*5W10MCM-*E***	87	37 / 11 / 8 / 44	6	94

a) Reaction conditions: 1-octene (5.0 mmol), THF (5 ml), 600 psi (CO / H_2=1/1), 80 ^oC, 16 h.
b) Determined by GC.
c) Determined by GC and ^1H NMR.
d) $P(OPh)_3$ (0.010 mmol) was added.
e) 110 ^oC, 3 h.

5.3.2 Hydroformylation of 1-octene by Rh-HPW_{12}-MCM-41 system. Effect of the temperature

The temperature of the reaction of hydroformylation of 1-octene has a strong effect on the conversion and the selectivity. The reaction was studied using the supported catalyst systems **Rh*3*2W10MCM-*M*** and **Rh^{B}*1*2W10MCM-*M*** formed by the impregnation of Rh(III) and Rh(I) complexes with HPW_{12} on MCM-41 in methanol (*M*) (Figures 5.1, 5.2 and 5.3). The reaction was conducted for 16 h with **Rh*3*2W10MCM-*M*** and **Rh^{B}*1*2W10MCM-*M*** and for 6 h with the rhodium (I) supported catalyst **Rh^{B}*1*2W10MCM-*M***. The results showed that maximum conversion in the reaction of hydroformylation of 1-octene catalyzed by **Rh*3*2W10MCM-*M*** (Figure 5.1) was 94 % at 80 ^{o}C after 16 h. It is important to note that no reaction was observed at 50 ^{o}C and the conversion at 60 ^{o}C was only 4 % with 67 % selectivity toward the linear aldehyde (**L**). As the temperature of the reaction was increased the conversion increased and the selectivity dropped.

The addition of water inhibited the reaction of hydroformylation of 1-octene and the conversion at 80^{o}C dropped from 94 % to 26 %. In addition, the use of $P(OPh)_3$ showed also negative effect on the reaction and the conversion dropped to 35 %. However, **Rh^{B}*1*2W10MCM-*M*** showed higher catalytic activity compared to **Rh*3*2W10MCM-*M*** especially at temperatures below 80 ^{o}C (Figure 5.2). Excellent conversion (94 %) was obtained at 80 ^{o}C and reached 96 % at 90 ^{o}C. Similar to the previous observation, the selectivity of the reaction towards linear aldehydes decreased with the increase of the temperature (Figure 5.2). The same reaction was studied with **Rh^{B}*1*2W10MCM-*M*** for the effect of the temperature for 6 h only (Figure 5.3).



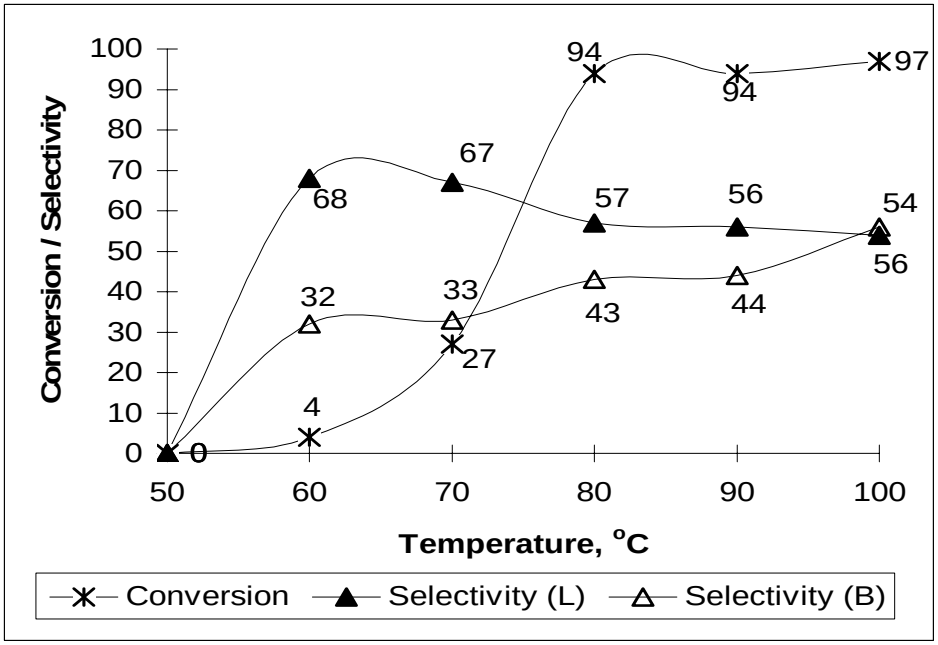
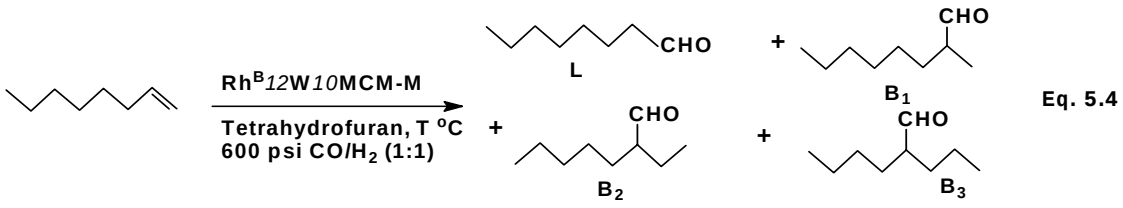


Figure 5.1. Hydroformylation of 1-octene by **Rh*3*2**W**10**MCM**-*M*. Effect of the temperature on the conversion and the selectivity. Reaction conditions: **Rh*3*2**W**10**MCM**-*M* (10 mg), 1-octene (5.0 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 16 h.



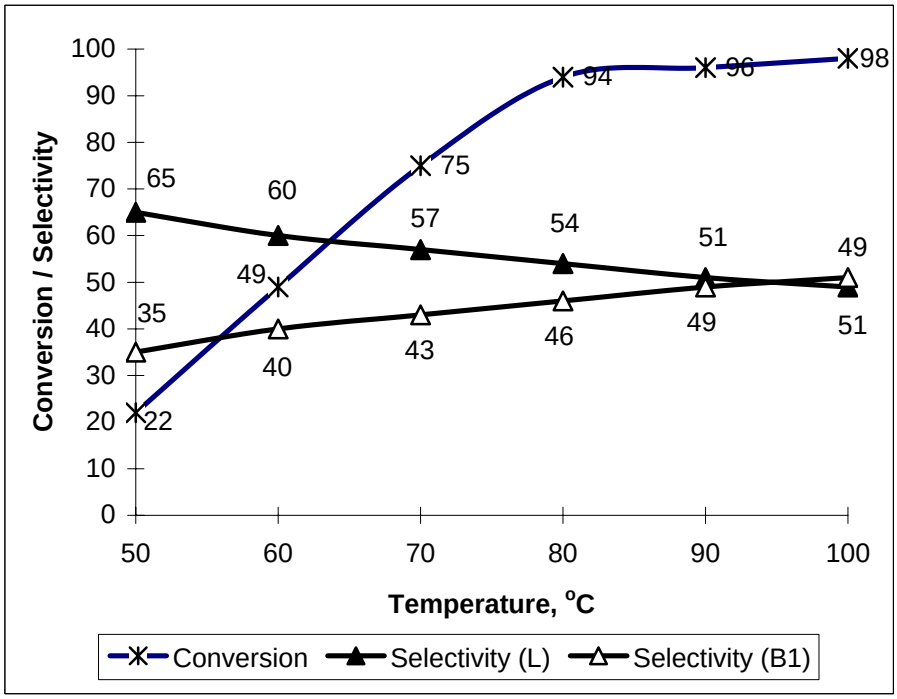
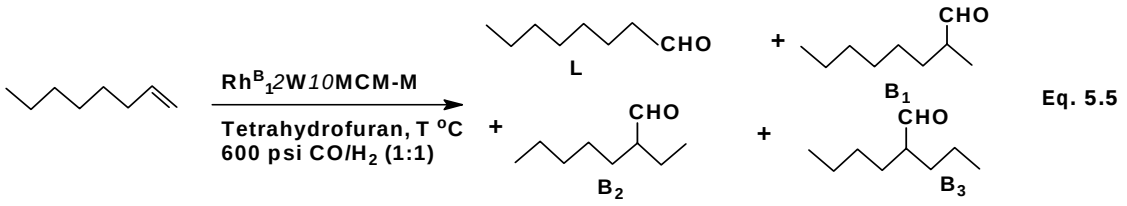


Figure 5.2. Hydroformylation of 1-octene by **Rh^{B}*1*2W10MCM-*M***. Effect of the temperature on the conversion and the selectivity. Reaction conditions: **Rh^{B}*1*2W10MCM-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), CO (300 psi), H_2 (300 psi), 16 h.



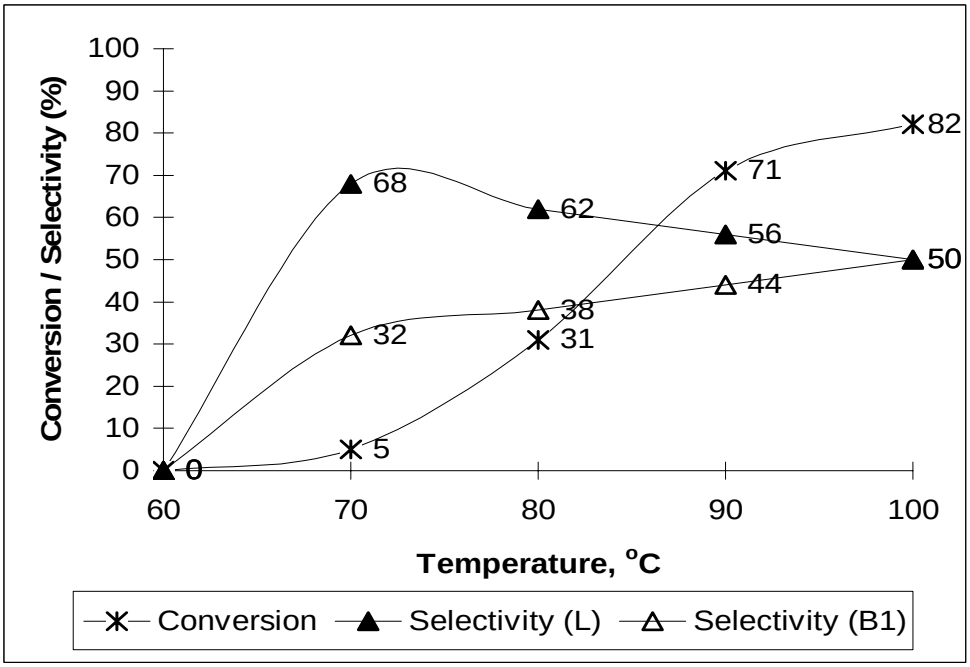


Figure 5.3. Hydroformylation of 1-octene by **Rh^{B}*1*2W10MCM-*M***.
Effect of the temperature on the conversion and the selectivity.
Reaction conditions: **Rh^{B}*1*2W10MCM-*M*** (10 mg), 1-octene (5.0 mmol),
THF (5 ml), CO (300 psi), H_2 (300 psi), 6 h.

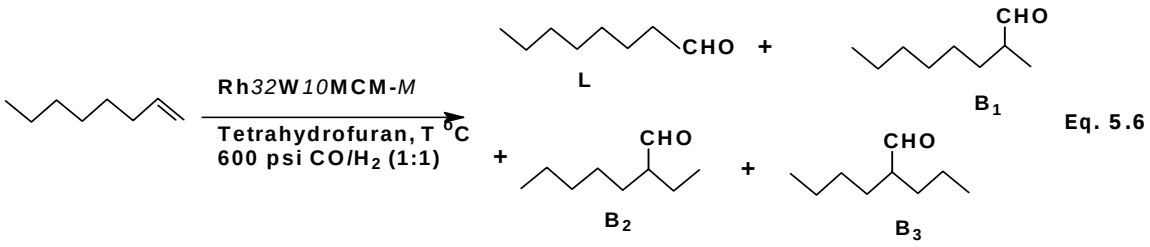
The conversion at 80 ^{o}C was 31 % only. The conversion increased to reach 71 % and 82 % at 90 ^{o}C and 100 ^{o}C, respectively. It appears that rhodium (I) supported catalysts were much active even at lower temperatures and shorter reaction time, while the selectivity was only slightly affected by the temperature and the type of rhodium catalyst.

5.3.3 Hydroformylation of 1-octene by supported catalyst. Effect of the reaction time and temperature

The hydroformylation of 1-octene was also carefully studied against reaction time and temperature (Tables 5.2 and 5.3). The effects of the reaction time and the temperature were investigated with **Rh***3*2W10MCM-*M* as a catalyst at 80 ^{o}C and 100 ^{o}C for the reaction time of 2-16 h (Table 5.2). The conversions were very low (<28 %) at 80 ^{o}C for the periods 2-8 h. However, a significant increase in the conversion (68 %) was observed after 12 h and a maximum conversion (94 %) was achieved after 16 h. At 100 ^{o}C the rate of the reaction of hydroformylation of 1-octene increased compared to the previous conditions. The selectivity of the reaction was not much affected by the temperature and the ratio of L / B was almost maintained between 1.4 and 1.6.

However, the hydroformylation of 1-octene by the rhodium (I) supported catalyst **Rh**^{B}12W10MCM-M showed much faster reactions at 80-100 ^{o}C reflected by the higher conversions compared to reactions catalyzed by **Rh***3*2W10MCM-*M* (Table 5.3). The conversions at 100 ^{o}C reached 82 %, 90 % and 94 % at 6 h, 8 h and 12 h, respectively. It is very important to note that the isomerization of 1-octene increased with the time and the temperature. For example, at 80 ^{o}C the amounts of 1-octene not isomerized were 46 %, 17 %, 15 %, 13 % and 11 % between 4-16 h of reaction (Table 5.3, entries 3,5,7,9,11). At

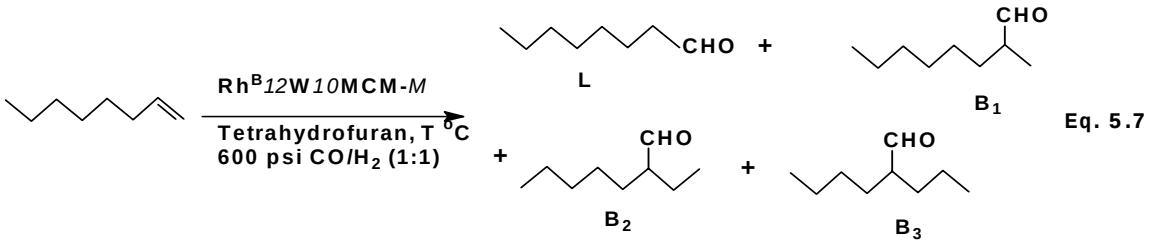
Table 5.2. Hydroformylation of 1-octene by Rh32W10MCM-M. Effect of the reaction time versus temperature.[a]



Entry	Time h	Conversion[b] %	T °C	Product Distribution[c] B_1 / B_2 / B_3 / L %	1-octene %	Octene Isomers %
1	2	2	80	30 / 0 / 0 / 70	98	2
2		8	100	27 / 0 / 0 / 73	54	46
3	4	6	80	32 / 0 / 0 / 68	88	12
4		32	100	35 / 4 / 7 / 54	18	82
5	6	12	80	36 / 2 / 4 / 58	76	24
6		58	100	34 / 6 / 8 / 52	4	96
7	8	28	80	36 / 3 / 5 / 56	32	68
8		76	100	34 / 7 / 9 / 50	4	96
9	12	68	80	36 / 4 / 6 / 54	24	76
10		90	100	33 / 8 / 10 / 49	5	95
11	16	88	80	37 / 5 / 8 / 50	17	83
12		98	100	32 / 10 / 12 / 46	4	96

a) Reaction conditions: **Rh*3*2**W**10**MCM**-*M* (10 mg), 1-octene (5.0 mmol), THF (5 ml), 600 psi (CO / H_2 = 1/1).
b) Determined by GC.
c) Determined by GC and ^{1}H NMR.

Table 5.3 Hydroformylation of 1-octene by Rh^{B}12W10MCM-M. Effect of the reaction time versus temperature.[a]



Entry	Time h	Conversion[b] %	T °C	Product Distribution[c] B_1 / B_2 / B_3 / L %	1-Octene %	Octene Isomers %
1	2	12	80	33/ 0 / 0 / 69	92	8
2		57	100	35 / 3 / 5 / 58	3	97
3	4	48	80	31/ 0 / 0 / 67	46	54
4		74	100	36 / 6 / 8 / 50	2	98
5	6	70	80	34 / 1 / 2 / 63	17	83
6		82	100	37 / 8 / 11 / 45	3	97
7	8	82	80	35 / 2 / 2 / 61	15	85
8		90	100	36 / 7 / 12 / 45	4	96
9	12	90	80	36 / 2 / 3 / 59	13	87
10		94	100	35 / 10 / 12 / 43	5	95
11	16	96	80	37 / 3 / 6 / 54	11	89
12		98	100	37 / 9 / 12 / 42	4	96
13[d]	6	58	80	36 / 1 / 2 / 61	20	80
14[d]		78	100	35 / 7 / 10 48	2	98

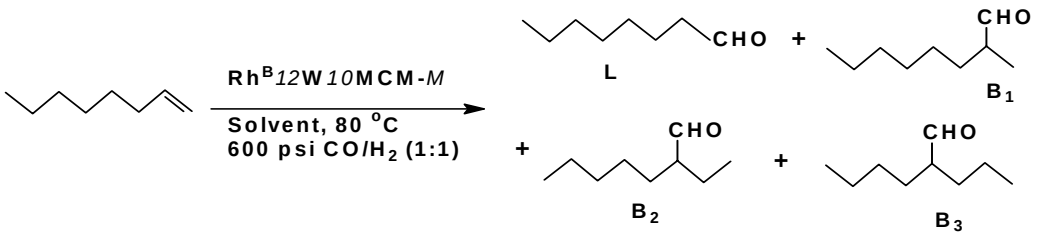
a) Reaction conditions: **Rh^{B}12W10MCM-*M*** (10 mg), 1-octene (5.0 mmol), THF (5 ml), 600 psi (CO/H_2 =1/1).
b) Determined by GC.
c) Determined by GC and ^1H NMR.
d) $P(OPh)_3$ (0.010 mmol) was added.

100 ^{o}C the rate of isomerization was much higher and the amounts of 1-octene not isomerized were 2-5 % only after 6-16 h (Table 5.3, entries 2,4,6,8,10,12). Rhodium (I) complexes are well known as catalysts enhancing the isomerization processes of alkenes [1].

The results obtained on the correlation of the reaction time versus temperature showed clearly the various options toward either very high conversion at higher temperature (100 ^{o}C) versus the high selectivity at lower temperature (80 ^{o}C) by fixing the reaction time at 6 h. Any increase in the reaction time will have an impact on both the conversion and the selectivity. Some additional experiments showed that the type of the heteropolyacid and the type of the rhodium (I) catalyst do not affect much this important correlation.

5.3.4 Hydroformylation of 1-octene by supported catalyst. Effect of the type of solvent

The type of solvent has a definite impact on the course of the reaction of the hydroformylation of 1-octene. Various solvents such as THF, DME, dioxane, acetone, MTBE, CH_2Cl_2, benzene, toluene, hexane and cyclohexane have been used in this study (Figures 5.4 and 5.5). Supported catalysts based on rhodium (III) and rhodium (I) were used. The results showed that there was no clear correlation of catalytic activity of the system with the polarity of the solvent. For instance, excellent conversions were obtained in THF, hexane, and cyclohexane, and no reaction or very poor conversions were observed with acetone, methyl ethyl ketone (MEK), CH_2Cl_2, MTBE, dioxane, benzene and toluene. These observations were made for both types of catalysts **Rh*3*2**W**10**MCM**-



Eq. 5.8

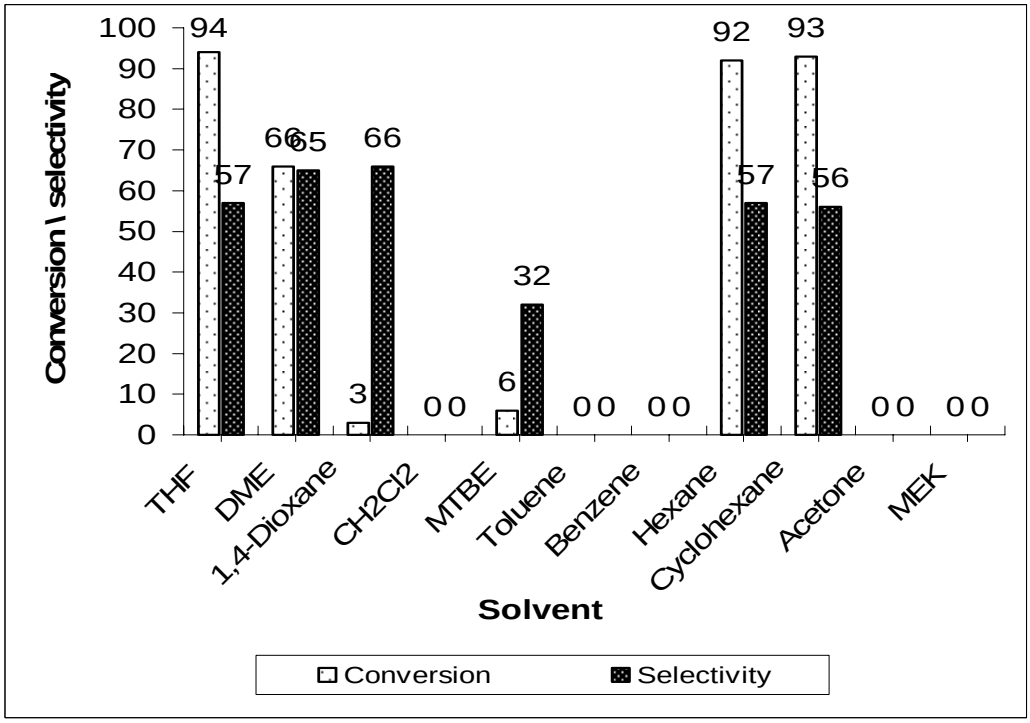
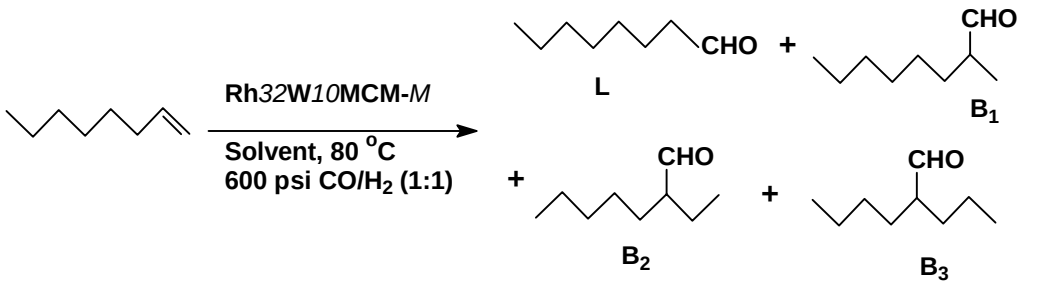


Figure 5.4. Hydroformylation of 1-octene by **Rh*3*2**W10**MCM**-*M*.
Effect of the type of solvent on the conversion and the selectivity in the linear aldehyde.
Reaction conditions: Catalyst **Rh*3*2W**10**MCM**-*M* (10 mg), 1-octene (5.0 mmol),
CO (300 psi), H_2 (300 psi), 80 ^{o}C, 16 h.



Eq. 5.9

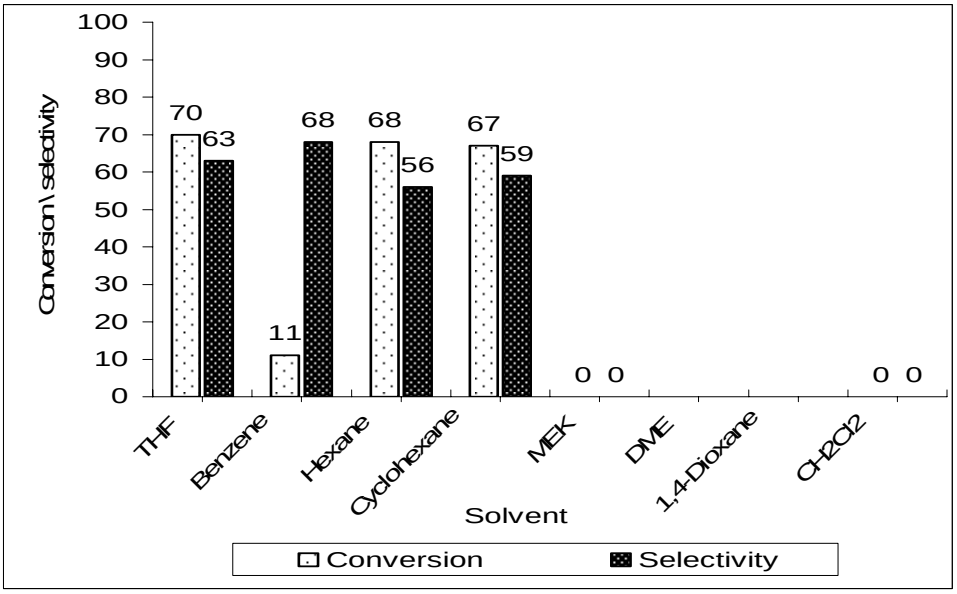


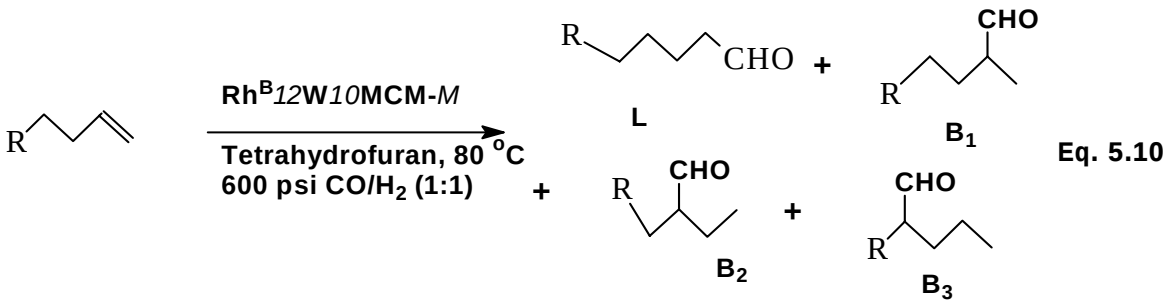
Figure 5.5. Hydroformylation of 1-octene **Rh^{B}*1*2W10MCM-*M***.
Effect of the type of solvent on the conversion and the selectivity in the linear aldehyde.
Reaction conditions: catalyst **Rh^{B}*1*2W10MCM-*M*** (10 mg), 1-octene (5.0 mmol),
CO (300 psi), H_2 (300 psi), 80 ^{o}C, 6 h.

E and **Rh^{B}*1*2W10MCM-*E*. However, the reaction was much faster with **Rh^{B}*1*2W10MCM-*E* in THF, hexane and cyclohexane as a solvent.

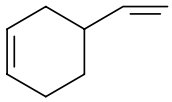
5.3.5 Hydroformylation of various terminal alkyl alkenes by Rh^{B}*1*2W10MCM-*E*.

The study of the optimization made with 1-octene showed that Rh^{B}12W10MCM-M is the active catalyst where the highest conversion was obtained at 80 ^{o}C and 16 h. Therefore, the hydroformylation of different terminal alkyl alkenes was realized using the catalyst system **Rh^{B}**12W10MCM-E in THF as a solvent at 80 ^{o}C and 16 h. The results are summarized in the Table 5.4. It has been observed that alkene with shorter alkyl chain, such as 1-heptene, was slightly less reactive than 1-octene under the same experimental conditions (Table 5.4, entry 1). The conversion was 72 % but the selectivity toward the aldehydes L+ B_1 was very high (98 %). Other long chain alkyl alkenes, such as 1-dodecene, 1-tetradecene and 1-hexadecene were converted to aldehydes (Table 5.4, entries 3-5), and the selectivity toward L + B_1 was also high (87-92 %). 4-Vinylcyclohexene was hydroformylated by the catalyst **Rh^{B}**12W10MCM-E (Table 5.4, entry 6). The reaction took place only on the terminal double bond (vinyl group) while the internal double bond (cyclohexene) stayed intact. The reaction was slower and the best conversion was obtained after 16 h was 56 %. The explored supported system that includes rhodium and heteropolyacid is also capable of converting various terminal alkyl alkenes with short and long alkyl chains into aldehydes. The reaction still lacking the high selectivity toward the linear aldehydes, but excellent overall results in terms of catalytic activity, conversion and total selectivity were obtained.

Table 5.4. Hydroformylation of various terminal alkyl alkenes.[a]



Eq. 5.10

Entry	Substrate	Conversion[b] %	Product Distribution[c] %		Alkenes[b] %	
			B_1 / L	$B_2+B_3+B_4$	1-Alkene	Alkenes Isomers
1	**1-Heptene**	72	35 / 63	2	21	79
2	**1-Octene**	96	37 / 54	9	11	89
3	**1-Dodecene**	80	36 / 56	8	33	67
4	**1-Tetradecene**	89	36 / 51	13	35	65
5	**1-Hexadecene**	84	35 / 52	13	39	61
6		56	16 / 84	-	-	-

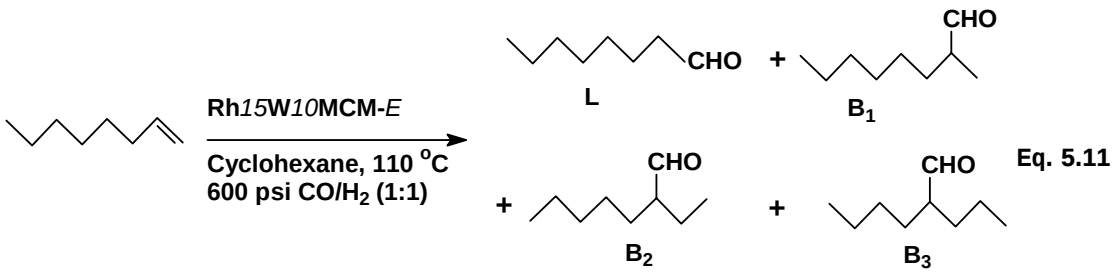
a) Reaction conditions: **Rh^B*12*W*10*MCM-*M** (10 mg), 1-octene (5.0 mmol), THF (5 ml), 80 ^oC, CO (300 psi), H_2 (300 psi), 16 h.
b) Determined by GC using anisole as internal standard.
c) Determined by GC and ^1H NMR.

5.3.6 Study of the catalyst recycling

The study of the recycling of the supported catalysts was realized in a similar manner to the hydroformylation of styrene (chapter 4, section 4.3.8). The hydroformylation of 1-octene was carried out with 50 mg of **Rh^{B}***1*5**W**10**MCM**-*E* or **Rh^{B}***1*5**MCM**-*E* using cyclohexane as a solvent. The results are summarized on Tables 5.5 and 5.6. Different recycling abilities were shown with **Rh^{B}***1*5**W**10**MCM**-*E* or **Rh^{B}***1*5**MCM**-*E*. The catalyst **Rh^{B}***1*5**W**10**MCM**-*E* has been recycled about eight times with acceptable to high conversions. The reaction time was different for the recycling experiments (Tables 5.5 and 5.6). The conversions of 87 % and 85 % were obtained at 3 h of reaction time (Tabe 5.5, entries 1-2). The conversions decreased at the same reaction time in the further cycles. However, if the reaction time was prolonged to 6 h, the conversions increased to 84 % (Table 5.5, entry 3). The catalytic activity of the catalyst decreases with number of cycles and more time was required to get the high conversions. For example, the conversions of 87 % and 64 % were obtained at the 5th and 6th cycles but after 12 h of reaction (Table 5.5, entries 5-6). The 7th and 8th cycles required more time as well (Table 5.5, entries 7-8). The products of the hydroformylation of 1-octene are nonaldehyde (linear L), 2-methyl octanaldehyde (branched B_1), 2-ethyl heptanaldehyde (branched B_2) and 2-propyl hexanaldehyde (branched B_3). The selectivity for the linear isomer ranges from 41 to 60 % and that of predominant branched isomer (2-methyl octanaldehyde) ranges from 34 to 39 %. The combined selectivity for the other two branched isomers ranges from 6- 21 % as shown in Table 5.5.

In order to assess the effect of HPA in the recycling process, we have made a comparative study by using the HPA free system (**Rh***15***MCM**-***E***) under the same

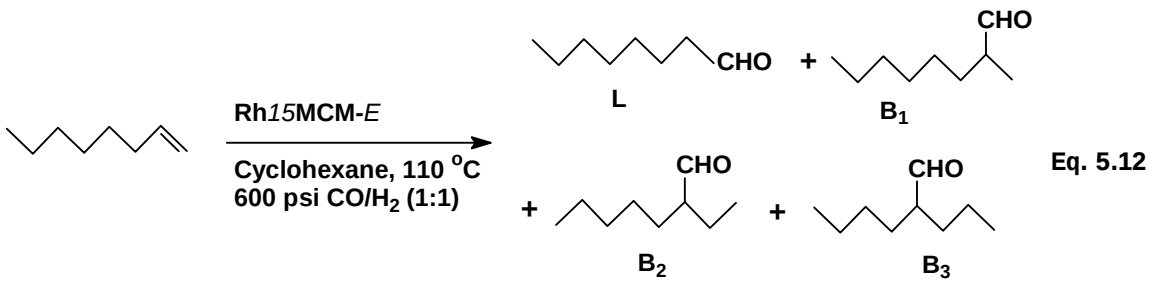
Table 5.5. Hydroformylation of 1-octene by Rh^{B}*15*W10MCM-*E*. Recycling of the catalyst.[a]



No. of cycles	Time h	Conversion %	Product Distribution[c] (%)			
			L	B_1	B_2	B_3
1	3	87	44	37	11	8
2	3	85	50	34	9	6
3	6	84	42	38	12	9
4	6	55	60	34	4	2
5	12	87	41	39	12	9
6	12	64	48	37	9	6
7	16	83	44	38	10	8
8	16	52	49	38	8	5

a) Reaction conditions: catalyst (50 mg), 1-octene (5.0 mmol), cyclohexane (5 ml), 600 psi (CO/H_2=1/1), 110 ^{o}C.
b) Determined by GC.
c) Determined by GC and ^{1}H NMR.

Table 5.6. Hydroformylation of 1-octene by Rh^{B}*15*MCM-*E*. Recycling of the catalyst.[a]



Eq. 5.12

No. of cycles	Time h	Conversion[b] %	Product Distribution[c] (%)			
			L	B_1	B_2	B_3
1	3	80	47	37	10	6
2	3	85	40	38	12	9
3	3	70	51	37	9	6
4	12	98	38	38	12	10
5	20	45	59	35	4	2

a) Reaction conditions: catalyst (50 mg), 1-octene (5.0 mmol), cyclohexane (5 ml), 600 psi (CO/H_2 = 1/1), 110 ^{o}C.
b) Determined by GC.
c) Determined by GC and ^{1}H NMR.

experimental conditions adopted for **Rh^{B}*1*5**W**10**MCM**-*E* (Table 5.6). The conversion of 1-octene by the end of 5th cycle has dropped to about 45 % even after running the reaction for 20 h compared to 98 % in case of **Rh*1*5**W**10**MCM**-***E*** after 12 h of reaction time.

These results showed again the advantage of using HPW_{12} along with rhodium catalysts anchored on MCM-41 in the process of the catalyst recycling. It is important to note that the recycling process with **Rh^{B}*1*5**W**10**MCM**-*E* or **Rh^{B}*1*5**MCM**-*E* in hexane showed similar trends to the process in cyclohexane as a solvent. Although, the use of THF in this experiment leads to excellent conversion of 1-octene but most of rhodium catalyst was leached out from the support and the catalyst could not be recycled.

The crystallinity of the MCM-41 support was monitored by X-ray powder diffraction. The X-ray patterns of recycled supported catalysts **Rh^{B}*1*5**W**10**MCM**-*E* are shown in Figure 5.6. The crystallinity of the MCM-41 support was maintained even after four cycles in the study of the catalyst recycling. These results showed the high stability of the system under the experimental conditions.

The supported catalysts were monitored by FT-IR spectrometry. The spectra of the systems that include MCM-41, HPW_{12}, $HRhCO(PPh_3)_3$, HPW_{12} supported on MCM-41, **Rh^{B}*1*5**W**10**MCM**-*E*, (Figure 4.1a-e) and the recycled supported catalyst **Rh^{B}*1*5**W**10**MCM**-*E* after 6 cycles (Figure 4.1f). The pure HPW_{12} spectrum with Keggin structure showed the following four important IR bands: 1082 (P-O), 988 (W=O), 800 (W-O-W) and 525 cm^{-1} (W-O-P) (Figure 4.1b) (142). It was also observed that the framework bands of Si-MCM-41 are 1235, 1084, 966, 801, 564 and 456 cm^{-1} (126) and overlap with those of HPW_{12} (127). The described IR spectra confirmed that the framework of MCM-41 remained intact even after six cycles.

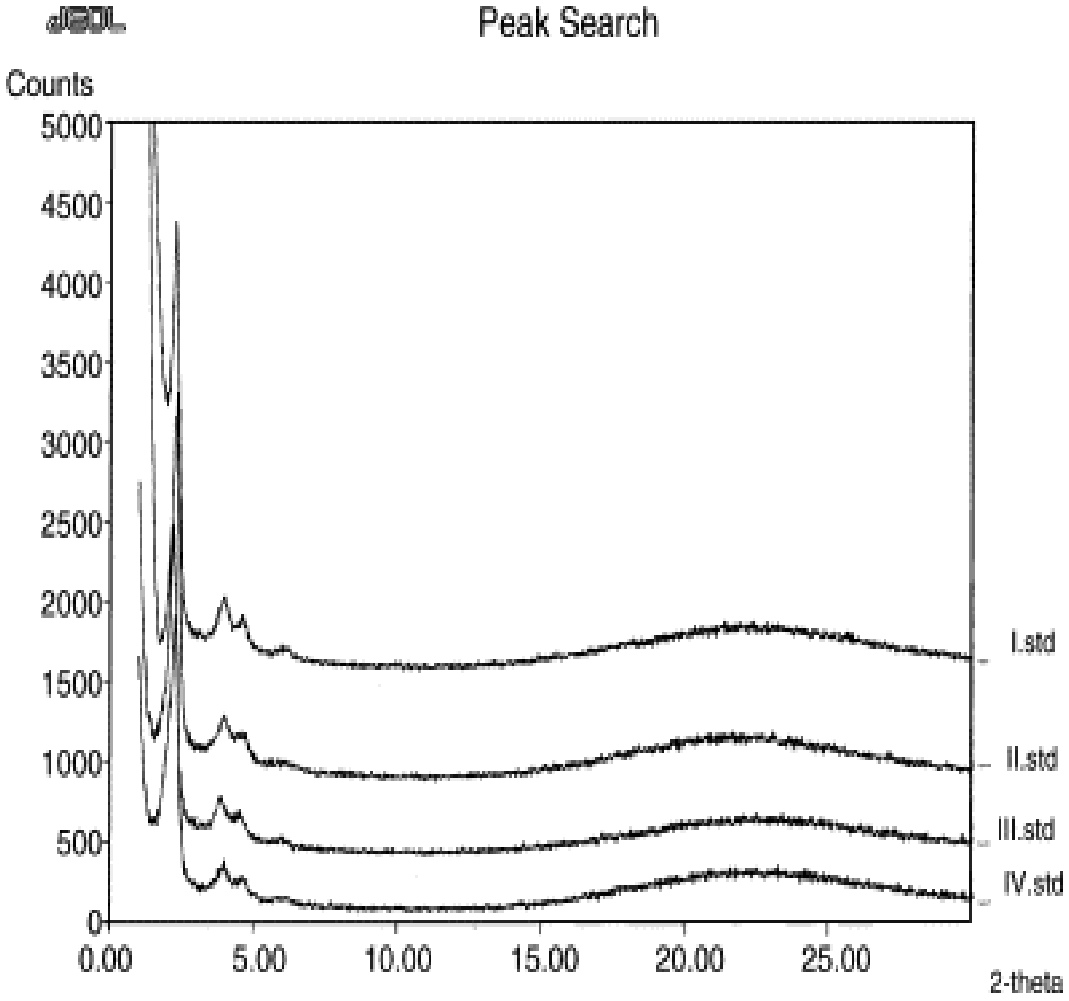


Figure 5.6. The X-ray powder diffraction patterns of recycled supported catalyst **Rh^{B}*1*5W10MCM-*E*** for 4 cycles.

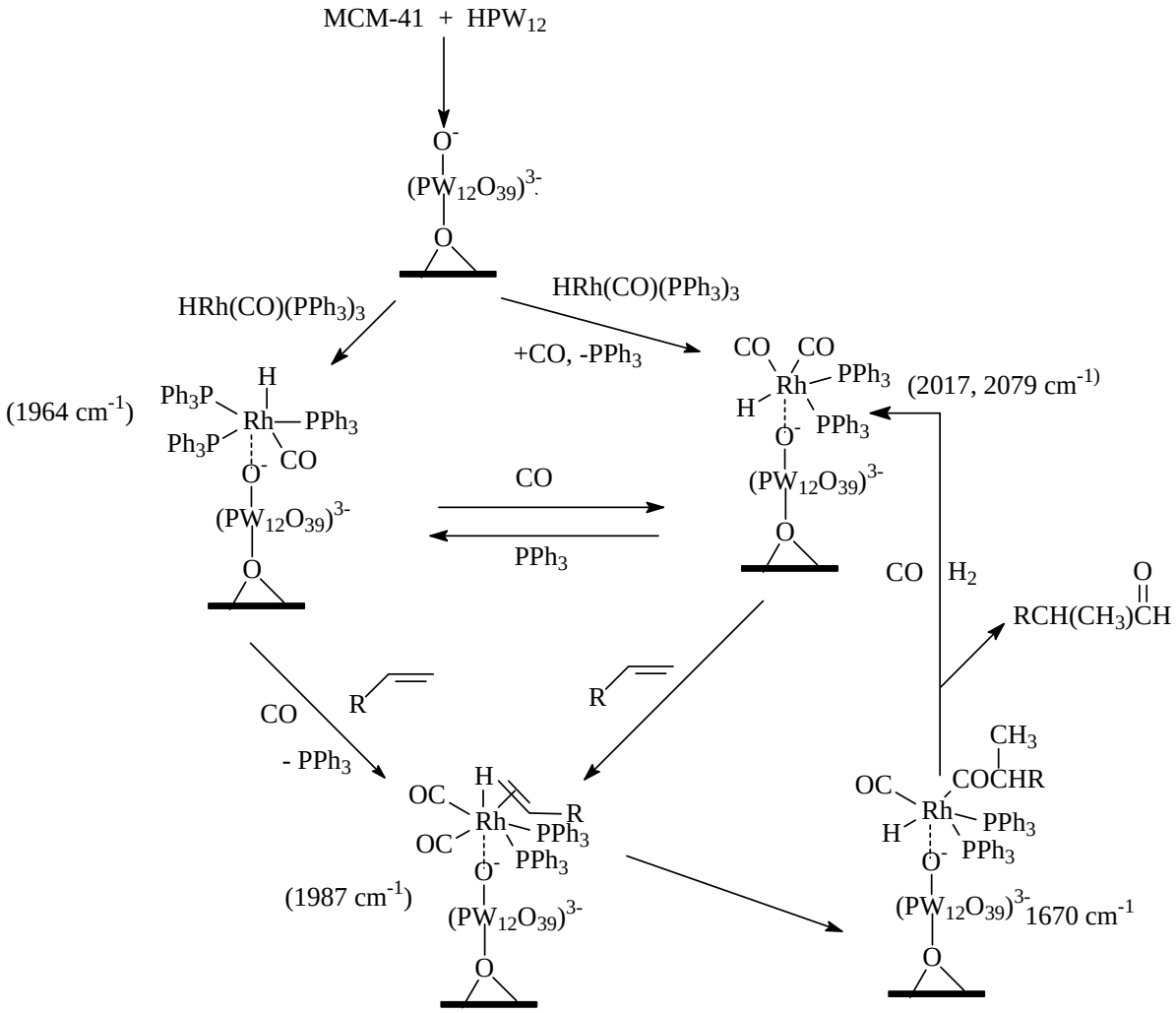
5.3.7 Proposed reaction mechanism for heterogeneous hydroformylation of alkenes

Keggin ions, $X^{n+}W_{12}O_{40}^{(8-n)-,}$ where X is phosphorous or silicon have T_d symmetry and feature tetrahedral XO_4 unit, at each vertex of which are three edge-shared MO_6 octahedral. The four M_3O_{13} trimetric groups are bonded to one another by a corner sharing of oxygen atoms (57). The charge in the $X^{n+}W_{12}O_{40}^{(8-n)-}$ anions is delocalized so that the oxygen atoms lying on the surface of the cluster are weakly nucleophilic. Oxygen alkylation is expected. Rh (I) cation, exemplified by $(Ph_3P)_2Rh(CO)^+$, may be stabilized in the solid state by the lattices provided by the negatively charged molecular metal oxide clusters (143).

The proposed reaction mechanism of the hydroformylation of alkyl alkenes is presented in the scheme 5.1.

The exact chemistry of the tethered moiety is not yet understood. Weak coordinate-covalent interaction similar between oxygen atoms of HPA and the Rh-atom of the $HRh(CO)(PPh_3)_3$ complex have been reported. This sort of ionic interaction fastens the Rh-complex tightly to the oxygen atoms of HPA tethered to the zeolite Y or MCM-41 matrix, thus restricting the complex from leaching out in the liquid phase (61,65).

The FT-IR is the most widely used method to characterize the supported rhodium through the study of the CO vibrational mode. The IR absorptions of CO and P-Rh in the pure Rh (I) carbonyl complex $HRh(CO)(PPh_3)_3$ are 1921 cm^{-1} and 515 cm^{-1}, respectively (Figure 4.1c) (51,128). However, the supported catalyst **Rh^{B}*1*5W10MCM-*E***, freshly prepared by the impregnation of $HRh(CO)(PPh_3)_3$ and HPW_{12} on MCM-41, showed a CO band of Rh–CO shifted to 1965 cm^{-1} (Figure 4.1e). When the same supported catalyst was treated with 600 psi of CO / H_2 for two hours at 110 ^oC, two absorptions appeared at 2017 and 2079 cm^{-1}, which correspond probably to the two gem-dicarbonyl. This



Scheme 5.1. Proposed reaction mechanism

observation is explained by the replacement of PPh_3 ligand by CO. Similar assignments were also made in previous reports (129,135).

However, the same catalyst **Rh^{B}*1*5W10MCM-*E*** showed at end of several cycles, new additional absorptions at 1714 and 1671 cm^{-1}. These two peaks are tentatively attributed to CO stretching in Rh–CO–Rh bridging and in the supported acyl rhodium species, respectively (Figure 4.1f) (128,134).

5.4 Conclusion

The hydroformylation of alkyl alkenes by the supported catalysts showed clearly that the rhodium (I) based catalyst **Rh^{B}*1*2W10MCM-*E*** was more active than **Rh*3*2W10MCM-*E*** in term of conversion at the same experimental conditions. The results showed no clear correlation between the catalytic activity and the polarity of the solvent. Excellent conversions were obtained in THF, hexane, and cyclohexane, and no reaction or very poor conversions were observed with acetone, MEK, CH_2Cl_2, MTBE, dioxane, benzene and toluene.

The addition of $P(OPh)_3$ in the reaction of the hydroformylation of 1-octene did not show any effect on the conversion, selectivity and the kinetics of the reaction and enhanced the leaching out of rhodium from the support.

The catalyst recycling showed clearly the role of the heteropolyacid on the catalytic activity of the impregnated rhodium (I) catalyst. **Rh^{B}*1*5W10MCM-*E*** or **Rh^{B}*1*5MCM-*E*** catalyzed efficiently the hydroformylation of 1-octene in cyclohexane as a solvent. However, the HPA containing system **Rh^{B}*1*5W10MCM-*E*** showed better recycling ability.

CHAPTER 6

6.0 SOLUBLE RHODIUM CATALYZED HYDROFORMYLATION OF POLYALKENES

6.1 Introduction

Utilization of catalytic chemical modification of polymers as a post polymerization process to improve and optimize the chemical and mechanical properties of the polymers or to introduce desirable functional groups into an existing polymer has been receiving increasing attention (68-71,74). The synthesis of specialty polymers containing certain desirable functional groups by metal catalyzed chemical modification of unsaturated polymers is an alternative route to the potentially difficult polymerization of monomers containing the desired functional groups. Some of the potential problems associated with the polymerization of functional monomers include:

(i) difficulty in polymerization

(ii) side reaction during the polymerization

(iii) difficulty in the synthesis of desirable monomers

(iv) in the case of copolymerization, unfavorable reactivity ratios (74).

The first report of the hydroformylation of polymers employed $Co_2(CO)_8$ (67). In order to accomplish hydroformylation, high temperatures and pressures were used which resulted in substantial gel formation rendering a useless product. Upon the development of hydridocarbonyltris(triphenylphosphine) rhodium (I), by Wilkinson (144), the reaction

conditions could be drastically modified and the hydroformylation of polymers were accomplished without of gel formation (4).

There are many applications for hydroformylated polymers, such as protective coatings (77-80), smooth and wrinkle-free films (81), and sizing for the glass fibers (82). The functionalized polyaldehyde products are key intermediates in the development of various polymer derivatives which form the basis for various novel material and component applications, such as the manufacture of automobile body components by reaction injection molding processing (145). Because of the reactivity of the aldehydes group, the hydroformylated products can be reacted via further reactions to produce nitrile alcohol, acetate and amine functionalities (146).

In this chapter the study of the hydroformylation of polybutadiene (PBD) using $Rh(CO)_2(acac)$ / $P(OPh)_3$ catalytic system is reported. The polymer products were characterized by infrared, ^{1}H NMR and ^{13}C NMR. The recycling experiment was also considered with [$Rh(CO)_2(acac)$ / tri(3-sulfonatophenyl)phosphine TPPTS catalytic system.

6.2 EXPERIMENTAL

6.2.1 Materials

The polymer used in this study is a low-molecular weight of polybutadiene (PBD). Analytical-grade toluene, obtained from Fisher Scientific Ltd., was used as received. $Rh(CO)_2(acac)$ was purchased from Strem Company and all other solvents were purchased from Sigma–Aldrich and were purified prior to usage.

^{1}H and ^{13}C NMR spectra were recorded on 500 MHz Joel 150 NMR machine. Chemical shifts were reported in ppm relative to tetramethyl silane (TMS) using $CDCl_3$.

6.2.2 General procedure for hydroformylation of polybutadiene

A typical experimental procedure is as follow: 0.5 g of polybutadiene, 0.005 mmol of $Rh(CO)_2(acac)$ and 0.060 mmol of $P(OPh)_3$ were dissolved in a mixture of 10.0 ml of dichloromethane placed in the glass liner of a 25 ml Parr autoclave. The autoclave was purged three times with carbon monoxide, pressurized with 600 psi of $CO + H_2$ (1:1 ratio) and then heated in an oil bath with temperature controller fixed at 80 ^{o}C. After 9 h the reaction mixture was cooled to room temperature, the products were identified by IR and NMR. The ^{1}H and ^{13}C NMR of the products gave excellent spectral data compared to authentic samples.

6.2.3 Characterization

All Fourier transform infrared (FTIR) spectra were obtained with a Bio-Rad FTS 3000X spectrometer. The IR samples were prepared through the casting of the polymer solution onto sodium chloride disks, which were then kept in the fume hood to evaporate the solvent. ^{1}H-NMR spectra of the polymer samples were obtained with a 500-MHz Joel 1500 NMR spectrometer. A comparison of the sum of the aldehyde proton and unsaturated proton integration and paraffin proton integration was used to calculate the degree of hydroformylation. The sample solutions were evaporated in a rotary evaporator. The rubber obtained was then dissolved in degassed $CDCl_3$ to prepare samples for NMR analysis. However, it was necessary to retain some small amount of the solvent in the

NMR samples because polyaldehyde would have been unstable if the solvent had been completely removed (146).

6.3 Results and discussion

6.3.1 NMR analysis of PBD

The polybutadiene used in these experiments are:

a. PBD60%Ph
b. PBD86%1,2-pred
c. PBD72%1,4-pred
d. PBD99%Ph

The **PBD60%Ph** polybutadiene, which is a mixture of 1,2- and 1,4-polybutadienes, was first analyzed by using ^{1}H NMR. The ^{1}H NMR is shown in the Figure 6.1a. Based on the integration of ^{1}H NMR spectra, the degree of unsaturation was estimated from the ratio of the integration of the olefinic proton to that of aliphatic proton. The olefinic protons are observed between 4.9-5.8 ppm range, while the paraffinic protons are observed in 0.8-2.2 ppm range. The specifications given by the manufacturer are: 60 % unsaturated, (45 % vinyl, 10 % trans- and 5 % cis-1,4- polybutadiene) with the number average molecular mass of (Mn) = 1800. The estimated percentage unsaturation is 57 % (44 % vinyl, 9 % trans 1,4- and 4 % cis 1,4-polybutadiene). The polymer is phenyl terminated.

The proton ^{1}H NMR spectrum of **PBD86%1,2-pred** is given in Figure A6.1b. The signals from 0.8 to 1.64 ppm are related to paraffin protons. The allylic protons occur at about 1.96-21.2 ppm, whereas the olefinic protons due to 1,2-PBD or a vinyl double bond

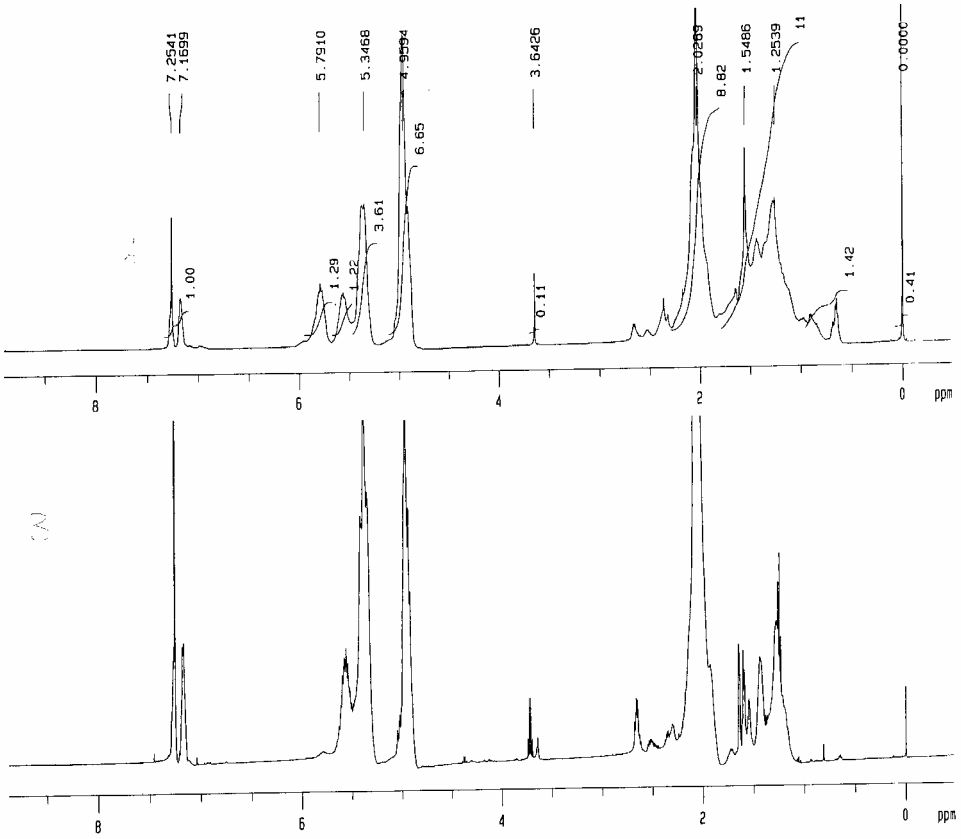


Figure 6.1

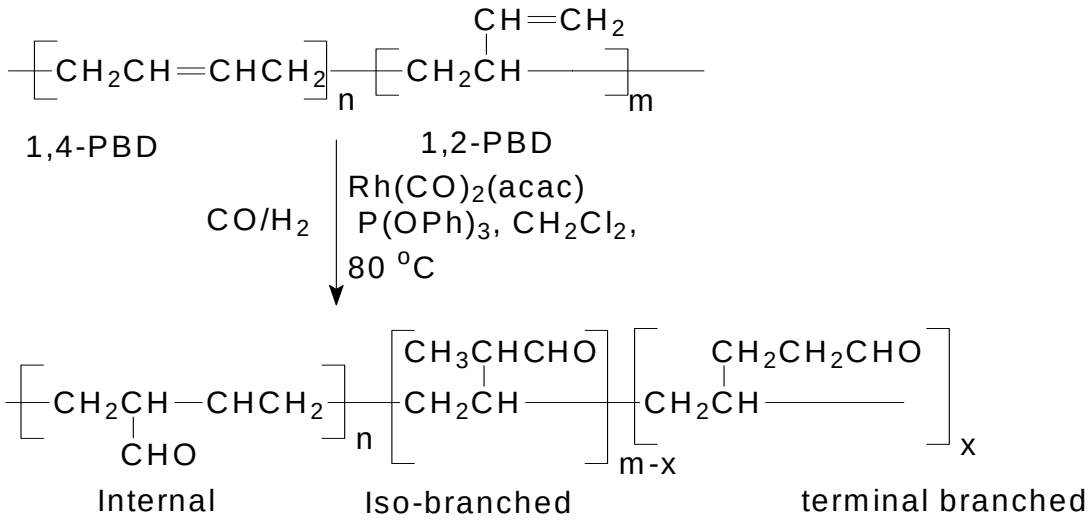
(A) ^{1}H NMR of PBD60%Ph (B) ^{1}H NMR of PBD99%Ph

occur from 4.7 to 5.6 ppm. The percentage of unsaturation was estimated as 86 % (65 % 1,2-polybutadiene and 21 % 1,4-polybutadiene). Similarly, the percentage unsaturation in **PBD72%1,4-pred** (Figure A6.1a) is 72 %, with 62 % trans 1,4- polybutadiene and 10 % vinyl polybutadiene. The signals from 1.0 to 2.0 ppm are associated with the paraffin protons. The allylic protons occur at about 2.2 ppm, whereas the olefinic protons due to 1,4-PBD or an internal double bond occur at 5.4 ppm, and those due to 1,2-PBD or a vinyl double bond occur from 4.7 to 5.6 ppm. **PBD99%Ph** is 99 % unsaturated, with 45 % vinyl, 35 % trans- and 19 % cis-1,4-polybutadiene (Figure 6.1b).

6.3.2 NMR analysis of PBD60%Ph hydroformylated products

Comparisons of the ^{1}H NMR spectra of the **PBD60%Ph** with the hydroformylated product are given in Figure 6.2 for the case where 58 % of the olefin units have been converted. The hydroformylation reaction conditions are: 0.5 g of **PBD60%Ph**, 0.005 mmol of $Rh(CO)_2(acac)$, 0.06 mmol of $P(OPh)_3$, 10.0 ml of dichloromethane at 600 psi ($CO / H_2 = 1/1$) (Table 6.1, entry 1). The spectrum depicted in Figure 6.2b show the two major aldehyde products and one minor aldehyde is present. The broad peak at 9.5 ppm and corresponding ^{13}C NMR shift at 204.6 ppm are assigned to the internal aldehyde associated with the hydroformylation of the 1,4-cis + 1,4-trans-polybutadiene chains. This value for the ^{13}C NMR shift is in an excellent agreement with the value given for the 2-ethylhexanal model compound (69).

The other major product appears as abroad peak at 9.7 relative to trimethyl silane, which correspond to ^{13}C NMR chemical shift of 202.1 ppm. This latter value agrees with



Scheme 6.1

the value of 201.9 ppm given to the butyraldehyde, which is the model compound for the addition of aldehyde to a branched terminal olefin. This peak would be associated with the hydroformylation of the 1,2-polybutadiene chains present in the PBD60%Ph. The small peak located at 9.6 ppm has a proton that is most likely associated with the iso-branched aldehyde. This product is formed in parallel with the terminal branched aldehyde from the 1,2-polybutadiene fraction of the PBD60%Ph.

On the basis of the above results, the following reaction occurs during the hydroformylation of **PBD60%Ph** under the indicated conditions. According to the scheme 6.1, the hydroformylation of the 1,2-polybutadiene produces both iso-branched and terminal-branched product through a series of parallel reactions. For the above mentioned reaction, the formation of the latter is highly favored. The hydroformylation of 1,4-polybutadiene unit of **PBD60%Ph** results in the formation of an internally branched aldehydes product. These observations are consistent with the results reported by Pruett and Smith (147) for the hydroformylation of monomer olefins.

The percentage conversion was provided by the integration of the ^{1}H NMR peaks

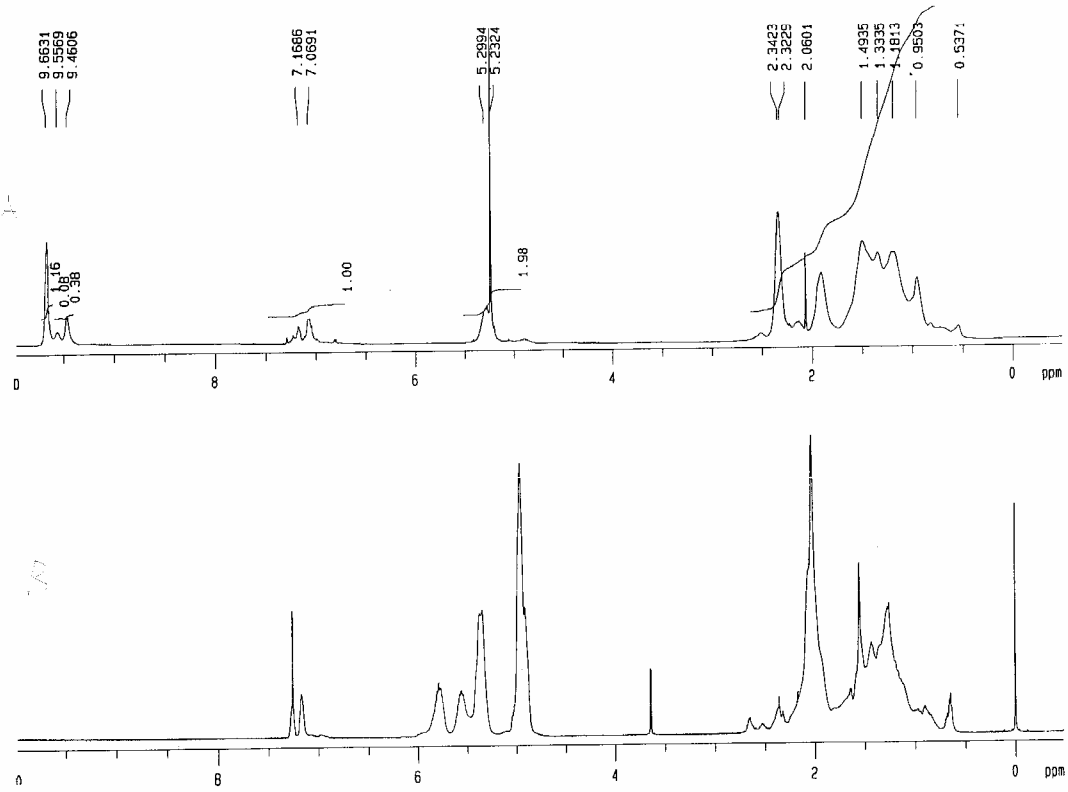


Figure 6.2

A) ^{1}H NMR of Partially hydroformylated **PBD60%Ph**

B) ^{1}H NMR of **PBD60%Ph**

in the aldehydes and the olefin region according to equation a. The conversion is 58 %, and a distribution of 82 %, 3 % and 15 % for terminal branched, iso-branched and internal aldehydes, respectively.

$$\%\,(\text{Hydroformylation}) = \frac{\text{integration aldehylic H}}{\text{integration (aldehylic H} + 0.5\text{olefinic H)}} \qquad \text{equation a}$$

6.3.3 NMR analysis of PBD86%1,2Pred hydroformylated products

The ^{1}H NMR spectrum of the **PBD86%1,2pred** and the hydroformylated products are compared in Figure 6.3. The reaction conditions used are given in Table 6.1. There are three possible hydroformylation products as shown in Scheme 6.1. A broad peak is observed at 9.7 ppm and ^{13}C NMR at 202.39 ppm, which corresponds to the terminal-branched aldehydes. The shoulder at 9.5 ppm is the iso-branched aldehydes. A confirmation of these assignments was obtained by the examination of the proton NMR spectra for the partially hydroformylated 1-hexene [9.5 (d), 9.7 (t)] and 3-hexene (9.5 (d)) (10). This suggests that hydroformylation of 1,2-polybutadiene under these condition occurs primarily through an anti-Markovnikov addition reactions (1).

The result shows that the percentage of olefins that have been hydroformylated is 77 % (with the distribution ratio of 78 % terminal branched, 16 % iso-branched and 6 % internal aldehydes. The percentage of the unsaturation of the product is estimated to be 10 %. A confirmation that the hydroformylation reaction is selective with negligible side reactions is provided by adding the percentage of unsaturation after the reaction to the

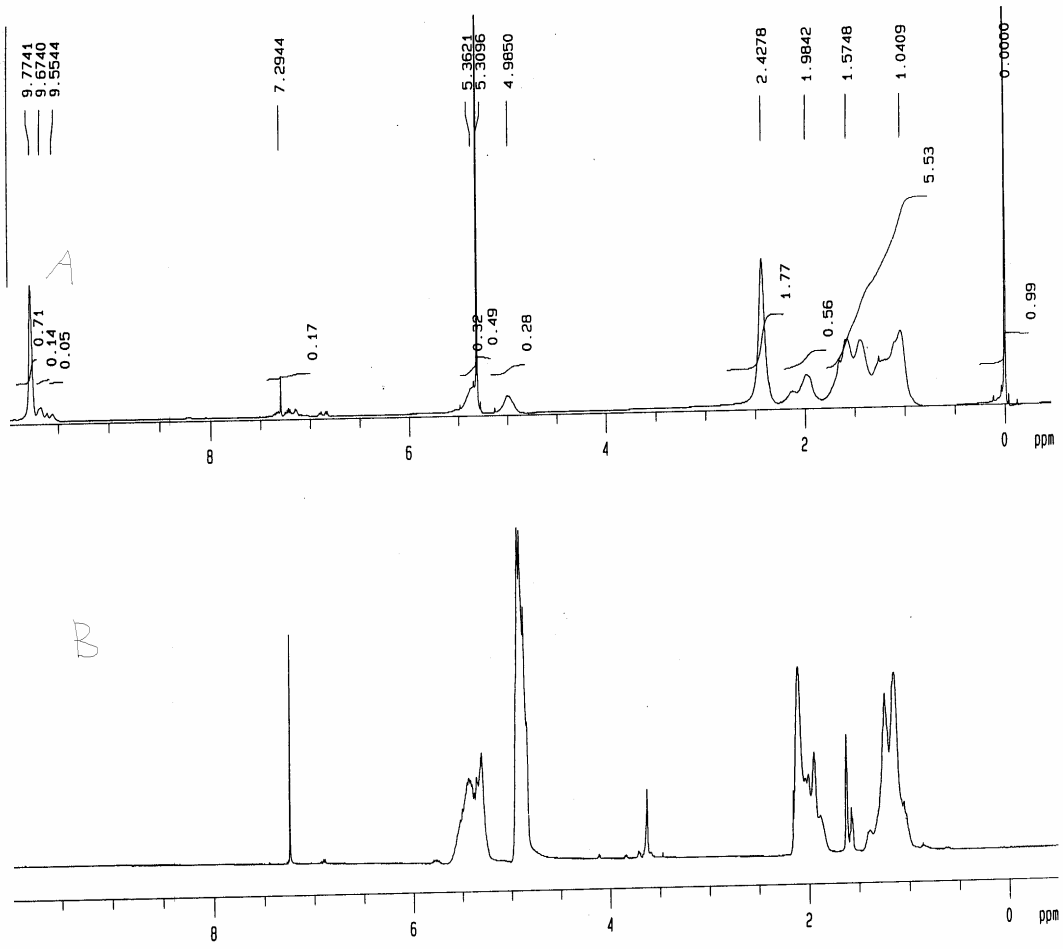


Figure 6.3

A) ^{1}H NMR of Partially hydroformylated **PBD86%1,2Pred**

B) ^{1}H NMR of **PBD86%1,2Pred**

percentage of olefin converted (77 % + 10 % = 87 %), this correspond to a difference of only 1 %, considering that the degree of unsaturation of the original polymer is 86 %.

6.3.4 NMR analysis of PBD72%1,4pred hydroformylated products

Figure 6.4 shows ^{1}H NMR spectra of **PBD72%1,4pred** and a partially hydroformylated product. The different aldehydes can be distinguished through the use of some model compounds. According to the data, the peaks attributable to aldehyde group are at 9.5 and 9.7 ppm. The peak at 9.5 ppm corresponds to the aldehyde group resulting from internal or anti-Markovnikov addition. The smaller peak at 9.7 ppm can be assigned to the aldehyde group, which may have resulted from the hydroformylation of 1,2-PBD as Markovnikov products (69,70,73).

The conversion is 53 % and the product distribution is 20 %, 6 % and 74 % for the terminal branched, iso-branched and internal aldehydes, respectively. The percentages (21 %) of the unsaturation after the reaction also indicate negligible side reaction.

6.3.5 NMR analysis of PBD99%Ph hydroformylated products

The ^{1}H NMR spectrum of the **PBD99%Ph** and the hydroformylated products are compared in Figure A6.2. The reaction conditions used are given in Table 6.1. There are three possible hydroformylation products as shown in Scheme 6.1. A broad peak in ^{1}H NMR spectra is observed at 9.7 ppm and at 202.39 ppm in ^{13}C NMR spectra, which corresponds to the terminal branched aldehydes. The shoulder at 9.6 ppm is the iso-branched aldehyde and the peak at 9.5 ppm was assigned to the internal aldehyde.

Integration of the ^{1}H NMR peaks in the aldehyde and olefin regions indicated that 53 % of the olefin units are hydroformylated. The product distribution includes terminal

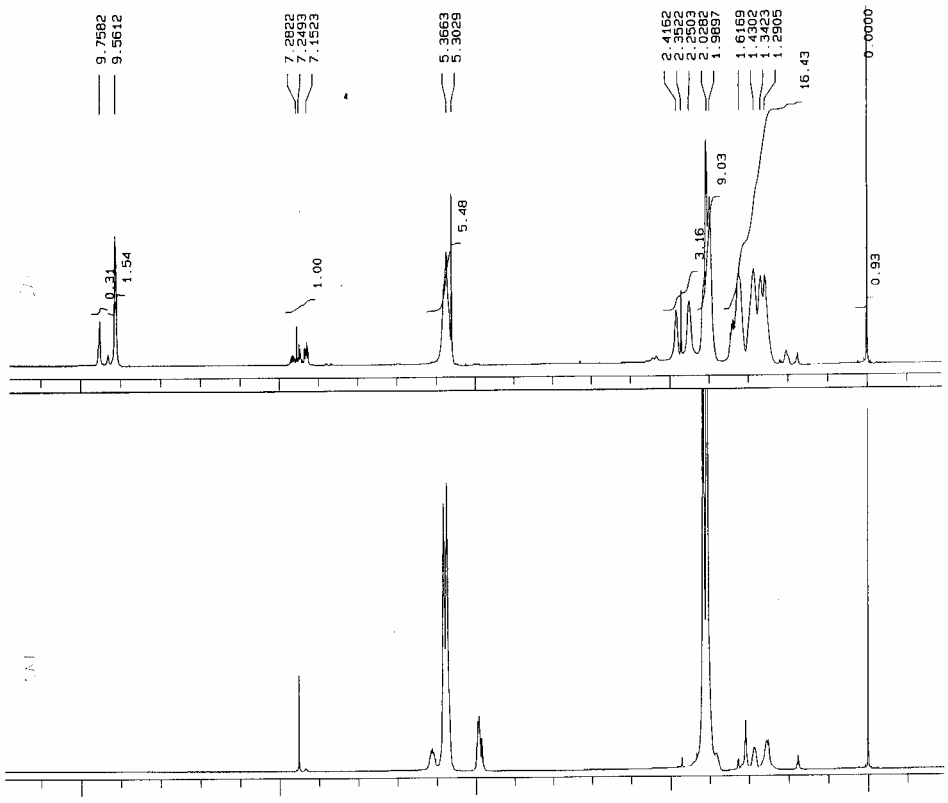


Figure 6.4

a) ^{1}H NMR of Partially hydroformylated **PBD72%1,4Pred**

b) ^{1}H NMR of **PBD72%1,4Pred**

branched aldehydes (54 %), iso-branched aldehydes (8 %) and internal aldehydes (38 %). The difference between the percentage unsaturation of the material and sum of the percentage conversion and the percentage unsaturation after the reaction (99 % - (53 % + 21%) = 25 %) suggested the possibility of other side reaction especially hydrogenation.

6.3.6 IR analysis for the hydroformylated products

IR spectra of **PBD72%1,4pred** and of the product of the partial hydroformylation are shown in Figure 6.5. It appears from the spectra that in addition to a decrease in the intensity of the bands at 912, 968, 995, and 1655 cm^{-1}, which can be attributed to C=C bonds, two new bands appeared at 1725 and 2700 cm^{-1}. The band at 1725 cm^{-1} is due to carbonyl (C=O) stretching vibrations, and that at 2700 cm^{-1} can be attributed to the COH stretching vibrations of the aldehyde group. No observation at 3500 cm^{-1} was made due to OH stretching. This result confirms that no appreciable products of the hydrogenation of aldehyde under the reaction conditions were observed.

6.3.7 Effect of reaction parameters

The effect of temperature on the reaction rate was studied over the rage of 60-100 ^{o}C. The following conditions were maintained throughout: 0.5 g of **PBD60%Ph**, 0.005 mmol of $Rh(CO)_2(acac)$, 0.06 mmol of $P(OPh)_3$, 10.0 ml of dichloromethane and 600 psi ($CO / H_2 = 1/1$) (Table 6.2, entries 1-4). The conversion of the olefin increases from 29 % at 60 ^{o}C to 59 % (almost complete conversion of all the olefin) at 100 ^{o}C. The products distribution remained almost the same through the whole range of temperature, i.e. more than 80 % of terminal branched aldehyde and about 15 % of internal aldehyde. The effect of temperature were also studied with triphenylphosphine and **PBD86%1,2Pred**. At 60

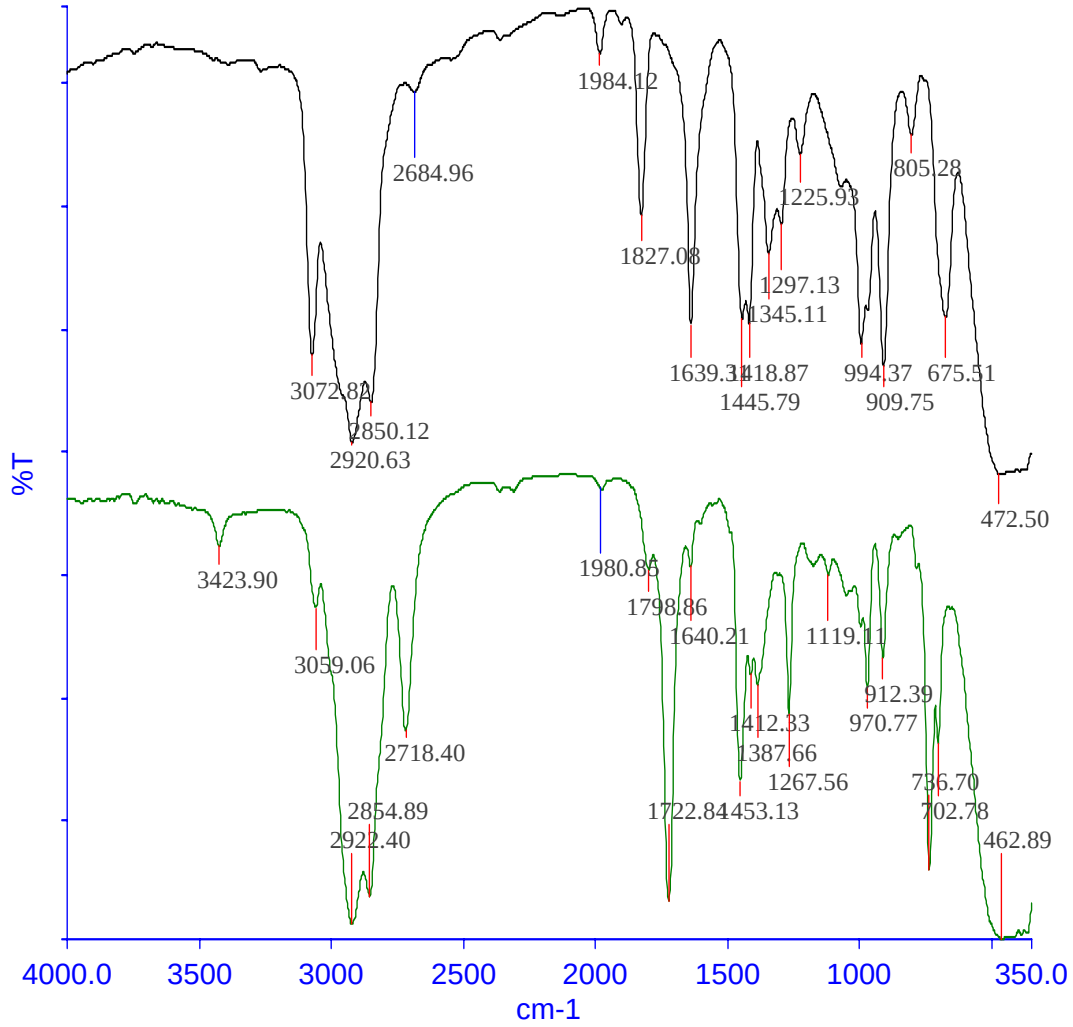


Figure 6.5. IR spectrum of **PBD72%1,4Pred** polybutadiene (lower spectrum) and its spectrum after the partial hydroformylation reaction (upper spectrum)

^{o}C, only 5 % conversion was obtained with almost 100 % selectivity for the terminal branched aldehyde. The conversion increases to 16 % at 70 ^{o}C and finally to 63 % at 80 ^{o}C, however, the selectivity for the terminal branched aldehyde decreases from 92 to 89 %, for 70 and 80 ^{o}C respectively (Table 6.1, entries 5-7).

Also, the effect of the addition of different ligands such as PPh_3, bis(2,4-di-tert-butyl)pentaerythritol diphosphite (alkanox P-24) (XXII) and $P(OPh)_3$ was studied. It was observed that $P(OPh)_3$ was the most efficient ligand where the hydroformylation of **PBD86%12Pred** led to a good conversion (77 %) and the selectivity of 78 %, 16 % and 6 % for terminal branched, iso-branched and internal aldehyde respectively (Table 6.1, entry 4). However, PPh_3 gave a total conversion of 63 % under the same conditions with slightly higher selectivity for terminal branched aldehyde (89 %, 6 % and 4 % for terminal branched, iso-branched and internal aldehyde, respectively). The bulky diphosphine ligand (XXII) gave 70 % conversion after 20 h with the best selectivity toward the terminal branched aldehyde (96 %), probably because of the inaccessibility of the bulky ligand to the internal double bond.

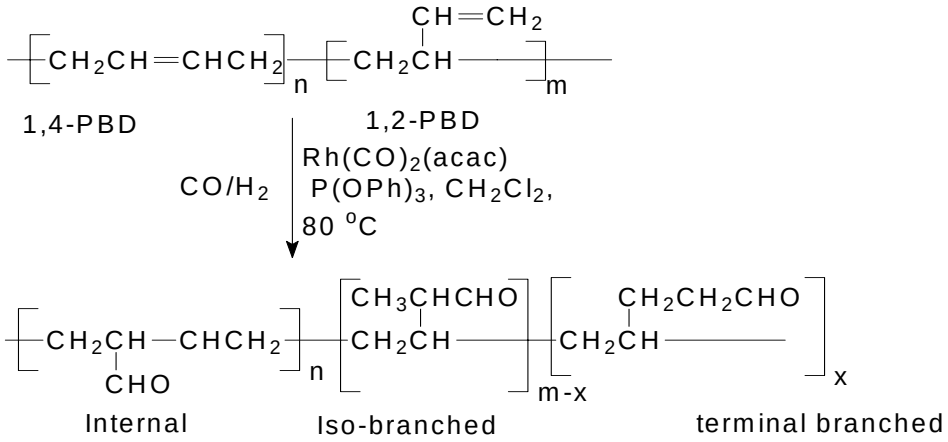
Three different solvents systems were studied to see the effect of solvent on the rate of the hydroformylation of polybutadiene polymers. The solvent used were dichloromethane, toluene and tetrahydrofuran. Table 6.1 shows a conversion of the hydroformylation of **PBD99%P**h with these three solvents. The percentage hydroformylation with THF is only 18 % with 88 % selectivity for the terminal branched and 12 % of internal aldehyde, no iso-branched aldehyde was observed. The highest conversion (85 %) was obtained with toluene with 44 %, 6 % and 45 % terminal branched, iso-branched and internal aldehyde, respectively.

Table 6.1 Catalytic hydroformylation of polybutadiene. [a]

Entry	Polymer	Ligand	Conv.[b] %	Unsat.[c] %	Term. %	Iso %	Inter. %
1	**PBD60%Ph**	**$P(OPh)_3$**	58	3	82	3	15
2	**PBD72%1,4pred**	$P(OPh)_3$	53	21	20	6	74
3	**PBD99%Ph**	$P(OPh)_3$	53	18	54	8	38
4	**PBD86%1,2Pred**	$P(OPh)_3$	77	10	78	16	6
5	PBD86%1,2Pred	PPh_3	63	24	89	6	4
6[d]	PBD86%1,2Pred	PPh_3	16	67	92	3	5
7[e]	PBD86%1,2Pred	PPh_3	5	80	100	-	-
8	PBD60%Ph	**PPh_3**	43	19	85	8	7
9[f]	PBD86%1,2Pred	**XXII**	70	14	96	2	2
10[f]	PBD60%Ph	**XXII**	53	9	88	5	7
11[g]	PBD99%Ph	$P(OPh)_3$	85	5	45	6	46
12[h]	PBD99%Ph	$P(OPh)_3$	18	nd	88	-	12

a) Reaction conditions: $Rh(CO)_2(acac)$ (0.005 mmol), 0.06 mmol ligand (0.03 mmol for XXII), CH_2Cl_2 (10.0 ml), 600 psi (CO / H_2=1/1), 80 ^oC, 8 h.
b) Determined by ^1H NMR.
c) Determined by ^1H NMR.
d) 70 ^oC
e) 60 ^oC
f) 10. ml Toluene
g) 10.0 ml THF

Table 6.2 Catalytic hydroformylation of polybutadiene.[a]



Entry	T °C	CO/H_2 psi	Conv.[b] %	Unsat.[c] %	Term. %	Iso %	Inter. %
1	**100**	300/300	59	2	82	3	15
2	**80**	**300/300**	58	3	82	3	15
3	**70**	300/300	39	23	81	7	13
4	**60**	300/300	28	28	83	10	17
5	80	**150/450**	38	17	81	6	13
6	80	**450/150**	46	10	71	8	18
7	80	**150/150**	45	6	79	6	15
8[d]	80	300/300	58	3	67	9	24

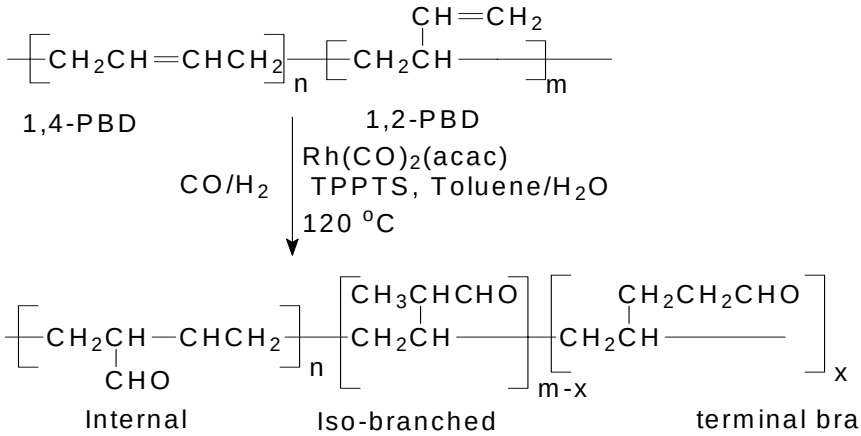
a) Reaction conditions: $Rh(CO)_2(acac)$ 0.005 mmol, $P(OPh)_3$ (0.06 mmol), PBD60%Ph 0.5g, CH_2Cl_2 (10.0 ml), 600 psi (CO / H_2=1/1), T °C, 8 h.
b) Determined by NMR.
c) Determined by ^1H NMR.
d) 20 h

The effect of the ratio of CO / H_2 at constant total pressure of 600 psi was studied with the catalytic system $Rh(CO)_2(acac)$ / $P(OPh)_3$ (Table 6.2). An increase in the ratio of CO / H_2 from 1/1 to 1/3 and 3/1 decreased the conversions of **PBD60%Ph** from 58 % to 38 % and 46 %, respectively (Table 6.2, entries 2,5,6). The % of internal aldehyde increases to 18 % when 3/1 CO / H_2 ratio was used. However, when the total pressure was reduced to half (150 / 150 psi CO / H_2) the conversion remained 45 % (Table 6.2, entry 7).

6.3.8 Biphasic Hydroformylation of polybutadiene: Recycling of the catalyst.

The aqueous/organic biphasic hydroformylation offered advantages in product isolation and catalyst recycling. The recycling experiments were carried out under constant conditions [120 ^oC, 600 psi of CO / H_2 (1:1), 16 h, 0.005 mmol of $Rh(CO)_2(acac)$ and 0.05 mmol of TPPTS]. After the reaction, the toluene phase that contained the products was separated from the reaction mixture by decantation. A fresh toluene and substrate was added to the aqueous phase containing catalyst. The rhodium catalysts can be easily recycled by this simple technique. Table 6.3 contains the results of the catalyst recycling for the hydroformylation of **PBD60%Ph**. The conversion of 50, 52 and 57 % were obtained for the cycle 1, 2 and 3, respectively. After the third cycles, a substantial gel formation was observed.

Table 6.3 Biphasic hydroformylation of PBD60%Ph. Recycling of the catalyst.[a]



Entry	No. of cycles	Conv.[b] %	Unsat.[c] %	term %	iso %	intern %
1	1	50	8	72	8	20
2	2	52	11	73	7	20
3	3	57	6	64	8	28

a) Reaction conditions: $Rh(CO)_2(acac)$ 0.005 mmol, TPPTS (0.06 mmol), PBD60%Ph 0.5 g, Toluene (7.0 ml) / H_2O (3.0 ml), 600 psi (CO / H_2=1/1), 120 ^oC, 16 h, 0.5 ml of methanol, 0.03 g PEO Mn 6000.

b) Determined by NMR.

c) Determined by ^1H NMR.

6.4 Conclusion

The catalytic hydroformylation of low-molecular weight 1,4-polybutadiene, 1,2-polybutadiene and a mixture of both 1,2- and 1,4-polybutadiene were achieved with $Rh(CO)_2(acac)$ / $P(OPh)_3$ in dichloromethane with conversions ranging from 18 to 77 %. A pronounced selectivity was observed with the hydroformylation of 1,2-polybutadiene. Under the hydroformylation conditions three possible products are formed, with iso-branched aldehyde as a minor product in all cases. This can be explained by the steric hindrance in the terminal unsaturation forcing the reaction towards anti-Markovnikov addition, although steric hindrance is present in the internal unsaturation, the high concentration of the internal double especially in **PBD72%1,4-Pred** and **PBD99%Ph** account for the internal hydroformylation.

CHAPTER 7

7.0 Conclusions

1. The results of the study showed clearly that the homogeneous catalytic system including $Rh_6(CO)_{16}$/HPA-W_{12}/CO/H_2/40^oC/16h (**system A**) and $Rh_6(CO)_{16}$/$P(OPh)_3$/CO/H_2/ 60^oC/6h (**system B**) in THF were active systems in the hydroformylation of styrene derivatives and alkyl alkenes. Excellent conversions of alkenes were observed. The role of the heteropolyacid HPA-W_{12} is probably through the formation of Rh-W-HPA intermediates and also in the formation and stabilization of the active rhodium carbonyl intermediate species at low temperature. The use of triphenyl phosphite **$P(OPh)_3$** was significant in terms of the improvement of the selectivity of the reaction. $P(OPh)_3$ is probably the most active ligand because it forms the active complex intermediates $Rh(CO)_xP(OPh)_y$ that are stable and active in THF as a solvent.

In the hydroformylation of 1-octene, the rhodium catalyst (XLII) modified with bulky diphosphite ligand (XXII) gives very high rate and selectivities. The regioselectivity is caused by the steric repulsion of the diphosphite that coordinate bisequatorially to the rhodium center. The same catalyst showed very low activity and selectivity for the internal alkenes.

2. The thermomorphic biphasic hydroformylation of 1-octene led to a very high conversion of alkenes and excellent yields of aldehydes and also a very attractive selectivity in the desired linear aldehydes. This selectivity depended mainly on the amount of $P(OPh)_3$, the total pressure of CO / H_2, the ratio of CO / H_2, the reaction time and the temperature. A variety of alkenes were converted into linear aldehydes at the optimum

reaction conditions that included: $P(OPh)_3$ / [Rh] = 12, 90 ^oC, CO / H_2 =100/100 psi and 1.5 h. DMSO / n-heptane and PC / n-heptane solvents pair were highly efficient especially in the recycling process where excellent conversion and selectivities were maintained.

3. A novel non-ionic water soluble phosphine ligand DPPPA-PEO has been synthesized by two-step ethoxylation of DPPPA. This phosphine ligand demonstrates the character of inverse temperature-dependant water solubility. The DPPPA-PEO catalyst formed in situ by $RhCl_3.3H_2O$ shows a high activity and excellent recycling efficiency in the aqueous-organic biphasic hydroformylation of 1-octene through the process of thermoregulated phase transfer catalysis.

4. The study of the hydroformylation of styrene and its derivatives by the heterogeneous catalysts led to interesting results. The impregnated catalysts based on rhodium (III) showed high catalytic activity in the presence of water. **Rh*3***2**W**10**MCM**-*M* was among the catalysts that gave the highest conversion at 80 ^oC. The amount of water added should be controlled because the use of excess of water did inhibit the reaction. The supported catalysts based on rhodium (I) were also very active and produce high conversions of styrene and its derivatives. The detailed study of the heterogeneous catalyst recycling showed clearly the role of the heteropolyacid in the supported catalyst. It is important to note that the influence of the heteropolyacid was in both catalyst systems that involve rhodium (I) and rhodium (III). The choice of the solvent of impregnation was very important in order to minimize the leaching. Cyclohexane as a solvent does not enhance the leaching of Rh (III) and Rhodium (I) supported catalysts. **Rh^{A}*1***5**W**10**MCM**-*E* catalyzed efficiently the hydroformylation of styrene with excellent conversion. It was very clear that the presence of HPA-W_{12} or HPA-Mo_{12} with Rh (I) or Rh(III) on the

support increased the catalytic activity of rhodium catalysts by improving the conversions of styrene and the recycling of the supported catalyst.

5. The hydroformylation of alkyl alkenes by the supported catalysts showed clearly that the rhodium (I) based catalyst **Rh^{B}*1*2W10MCM-*E*** was more active than **Rh*3*2W10MCM-*E*** in term of conversion at the same experimental conditions. The results showed no clear correlation between the catalytic activity and the polarity of the solvent. Excellent conversions were obtained in THF, hexane, and cyclohexane, and no reaction or very poor conversions were observed with acetone, MEK, CH_2Cl_2, MTBE, dioxane, benzene and toluene.

The addition of $P(OPh)_3$ in the reaction of the hydroformylation of 1-octene did not show any effect on the conversion, selectivity and the kinetics of the reaction and enhanced the leaching out of rhodium from the support.

The catalyst recycling showed clearly the role of the heteropolyacid on the catalytic activity of the impregnated rhodium (I) catalyst. **Rh^{B}*1*5W10MCM-*E*** or **Rh^{B}*1*5MCM-*E*** catalyzed efficiently the hydroformylation of 1-octene in cyclohexane as a solvent. However, the HPA containing system **Rh^{B}*1*5W10MCM-*E*** showed better recycling ability.

6. The catalytic hydroformylation of low-molecular weight 1,4-polybutadiene, 1,2-polybutadiene and a mixture of both 1,2- and 1,4-polybutadiene were achieved with $Rh(CO)_2(acac)$ / $P(OPh)_3$ in dichloromethane with conversions ranging from 18 to 77 %. A pronounced selectivity was observed with the hydroformylation of 1,2-polybutadiene. Under the hydroformylation conditions three possible products are formed, with iso-branched aldehyde as a minor product in all cases. This can be explained by the steric

hindrance in the terminal unsaturation forcing the reaction towards anti-Markovnikov addition, although steric hindrance is present in the internal unsaturation, the high concentration of the internal double especially in **PBD72%1,4-Pred** and **PBD99%Ph** account for the internal hydroformylation.

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Appendices

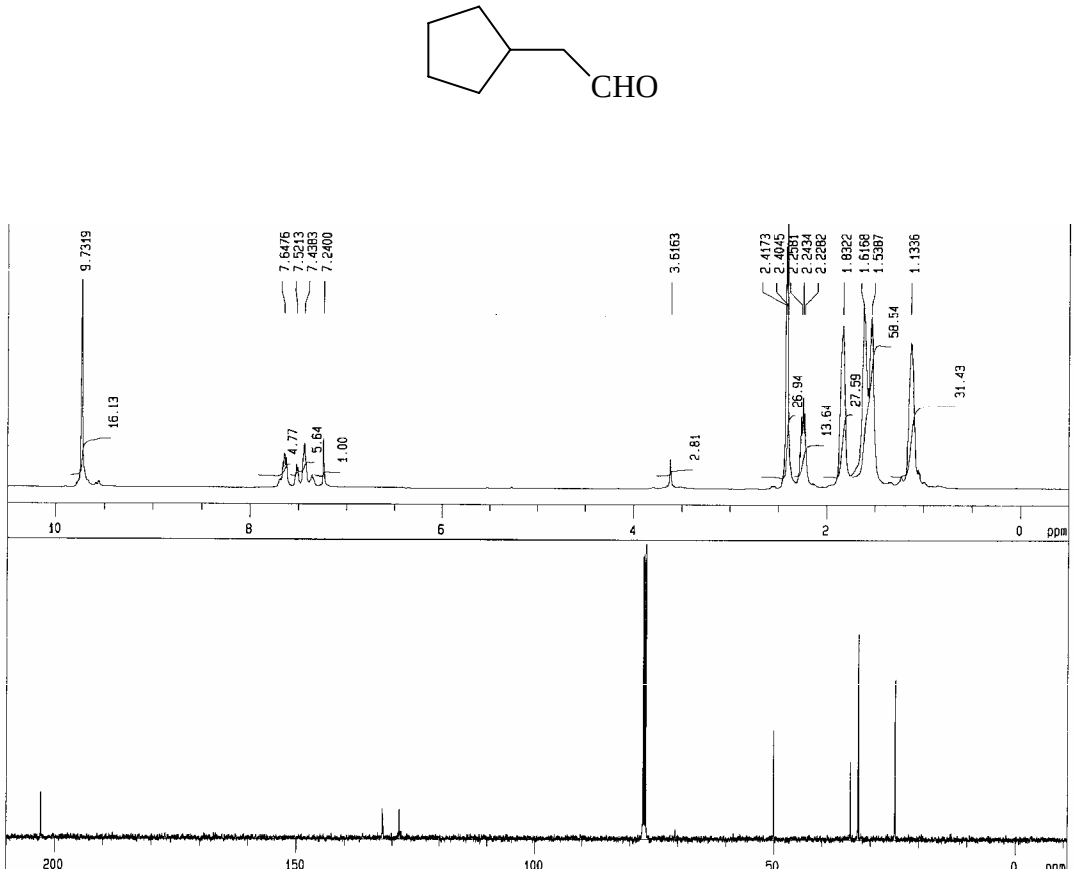


FIGURE A2.1

^{1}H NMR of 2-cylopentyl ethanal **L (XXV) (upper spectrum) and its ^{13}C MNR spectrum (lower spectrum)**

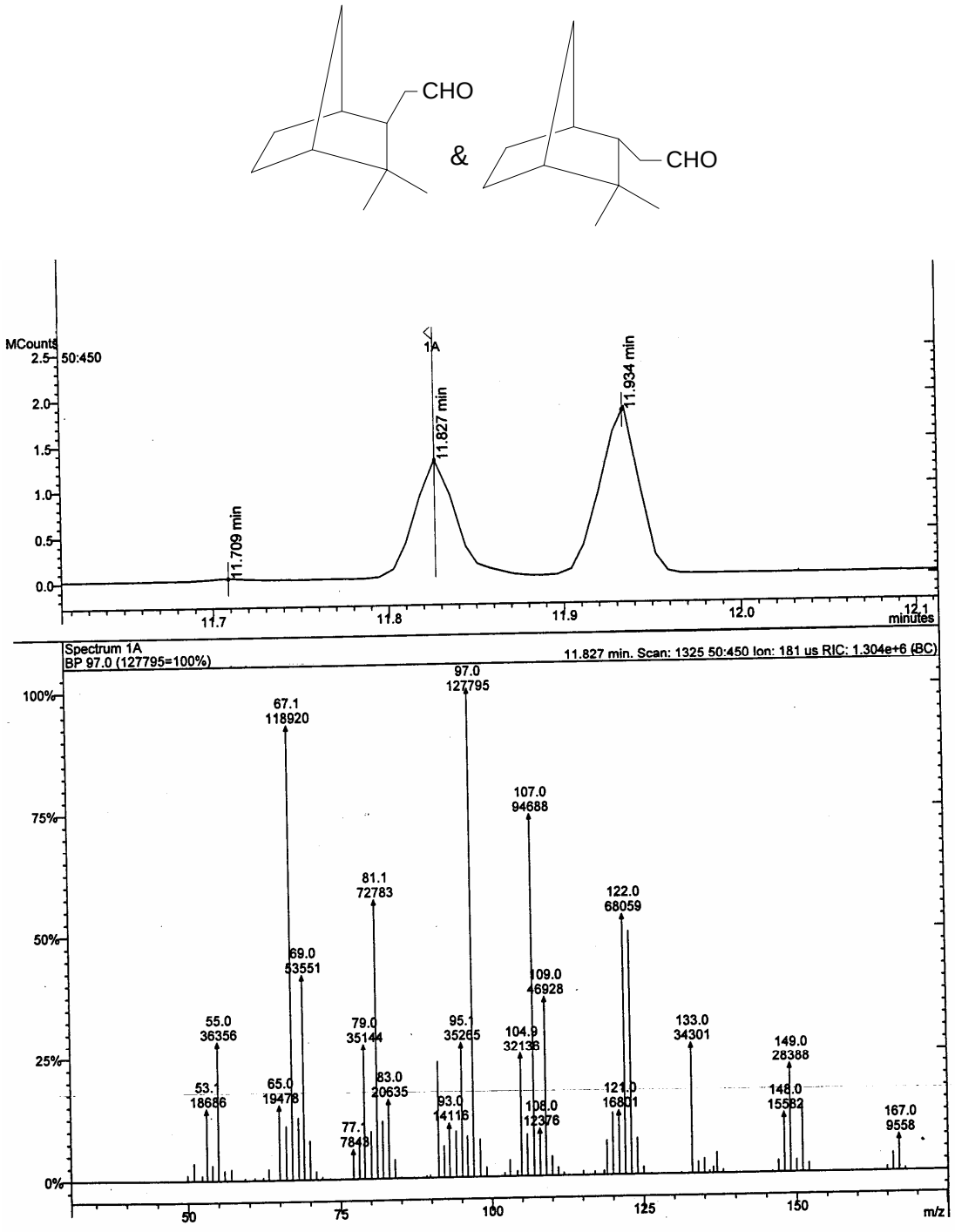
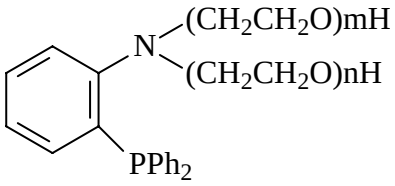


Figure A2.2

GC-MS of hydroformylated camphene **(XLI and XL)**



PEO-DPPPA (n + m = 42)

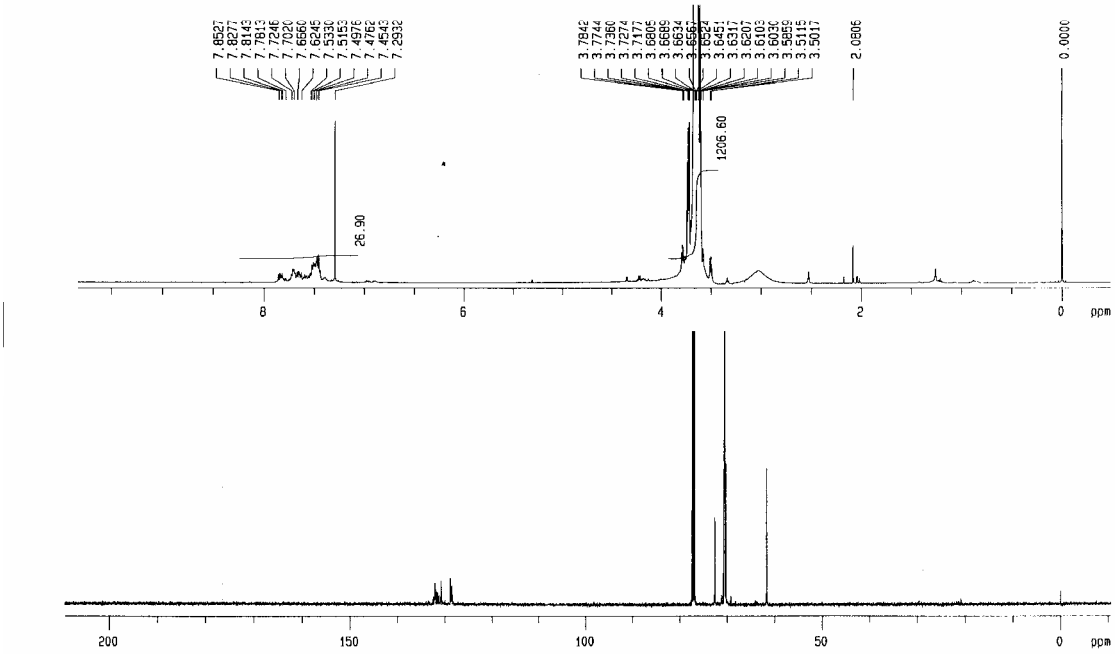


FIGURE A3.1

^{1}H NMR DPPPA-PEO (upper spectrum) and ^{13}C NMR of DPPPA-PEO (lower spectrum)

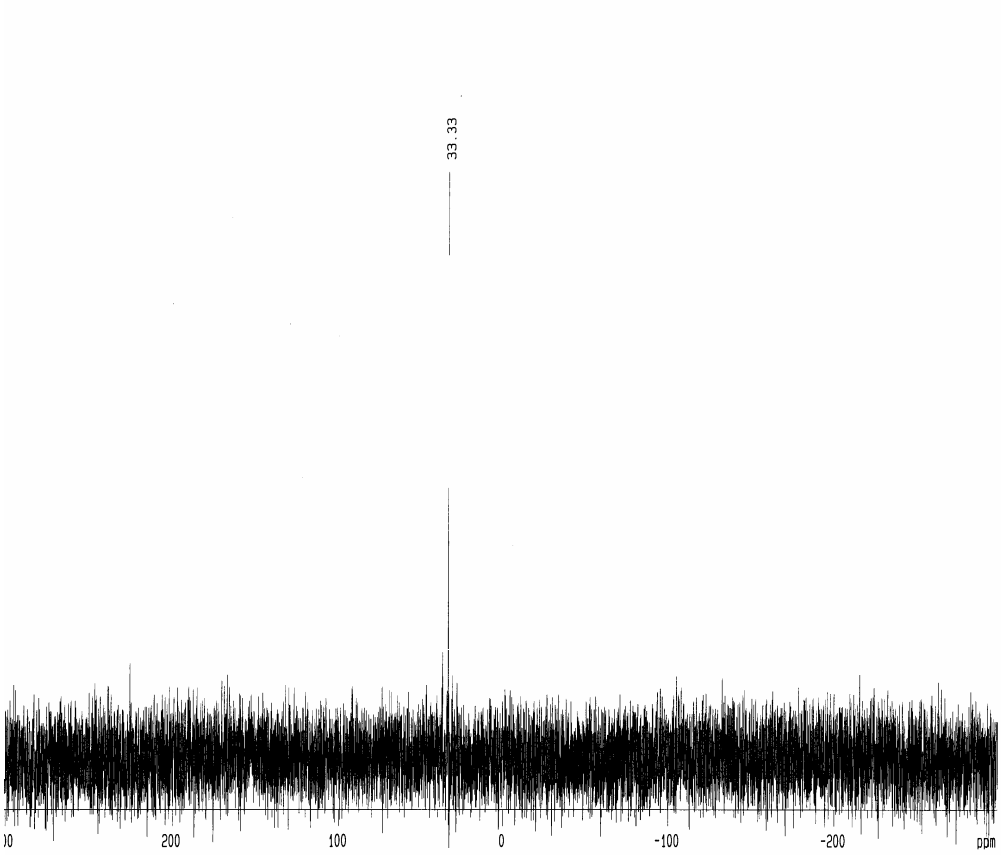


FIGURE A3.2

^{31}P NMR of **[Rh(CO)(μ-imid)(DPPPA-PEO)]$_2$**

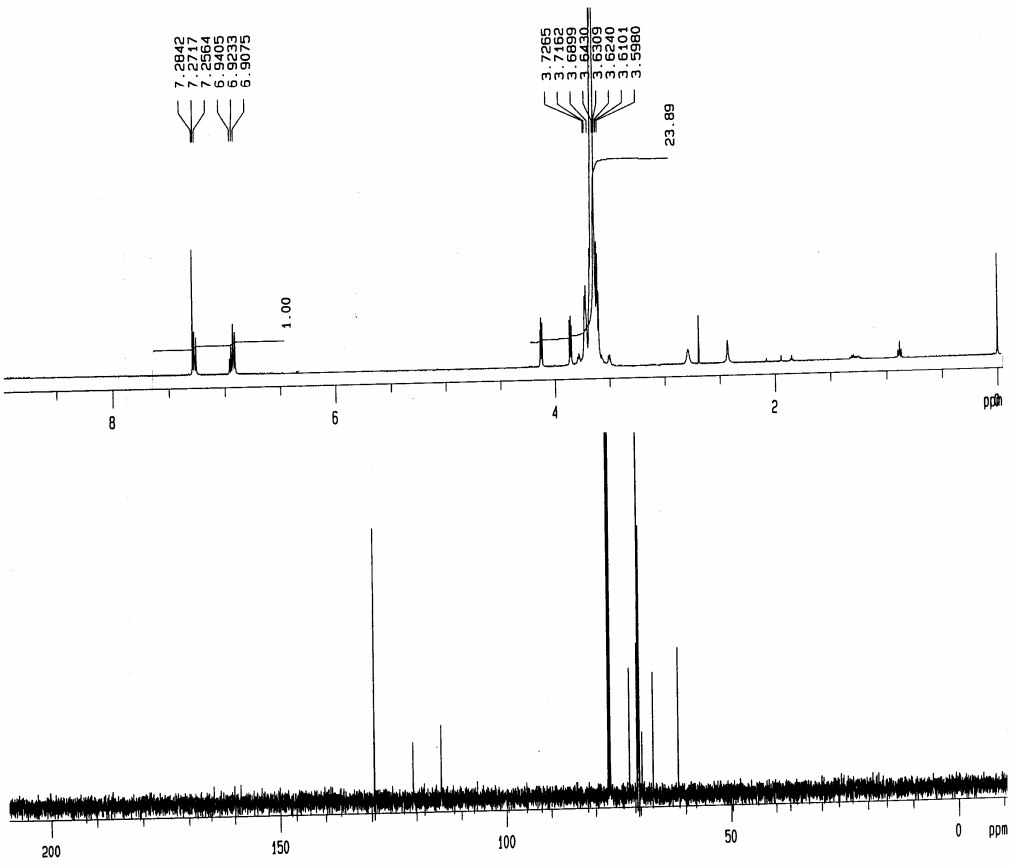


FIGURE A3.3

^{1}H NMR Ph-$(OCH_2CH_2)_{38}$-OH (upper spectrum) **and its ^{13}C NMR** (lower spectrum)

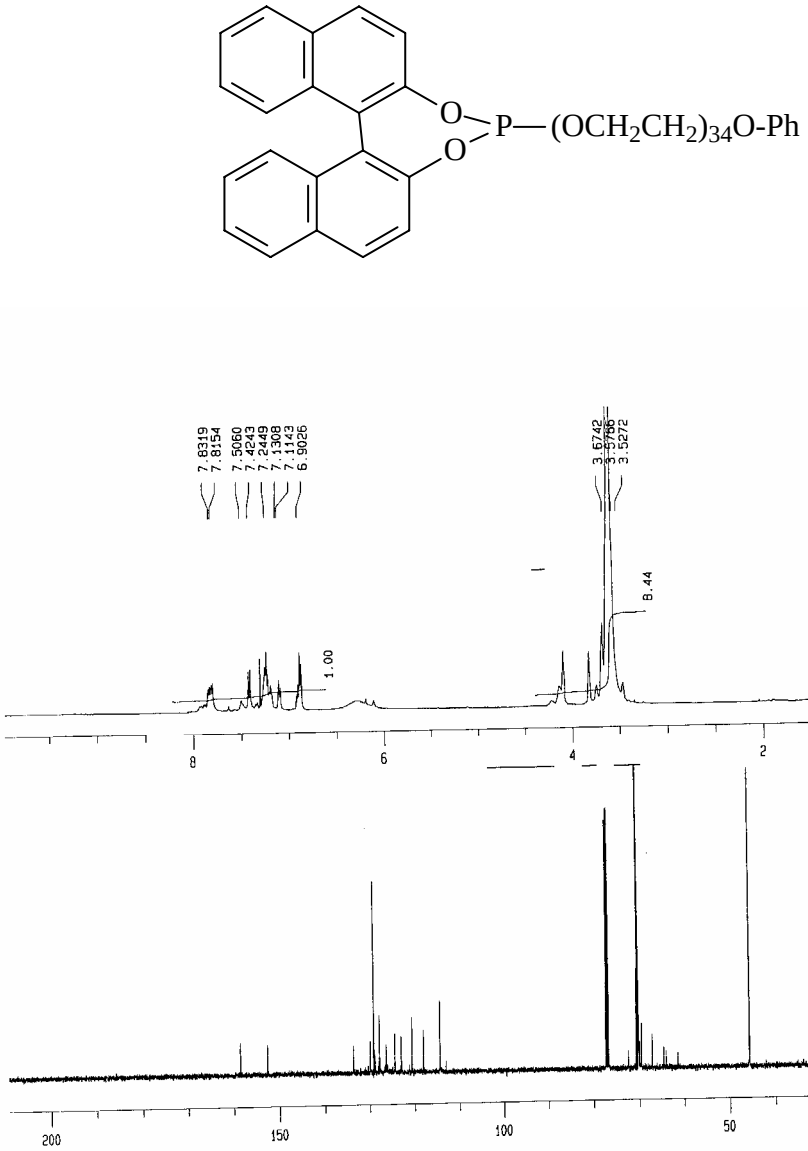


FIGURE A3.4

^{1}H NMR binaphthyl phosphite polyethylene oxide (upper spectrum) **and its ^{13}C NMR** (lower spectrum)

Table A4.1. The analysis of the percentage loading of rhodium on supported catalysts by ICP.

Entry	**Sample Name**	**Rh % w/w calculated**	**Rh % w/w found**	**W (or Mo) % w/w calculated**	**W (or Mo) % w/w found**
1	**Rh***15*W*10*Y-E	0.56	0.44	6.5	1.76
2	**Rh***15*W*10*MCM-E	0.56	0.48	6.5	0.90
3	**Rh***15*Mo*10*MCM-E	0.56	0.32	4.2	1.12
4	**Rh***15*MCM-E	0.56	0.21	-	-

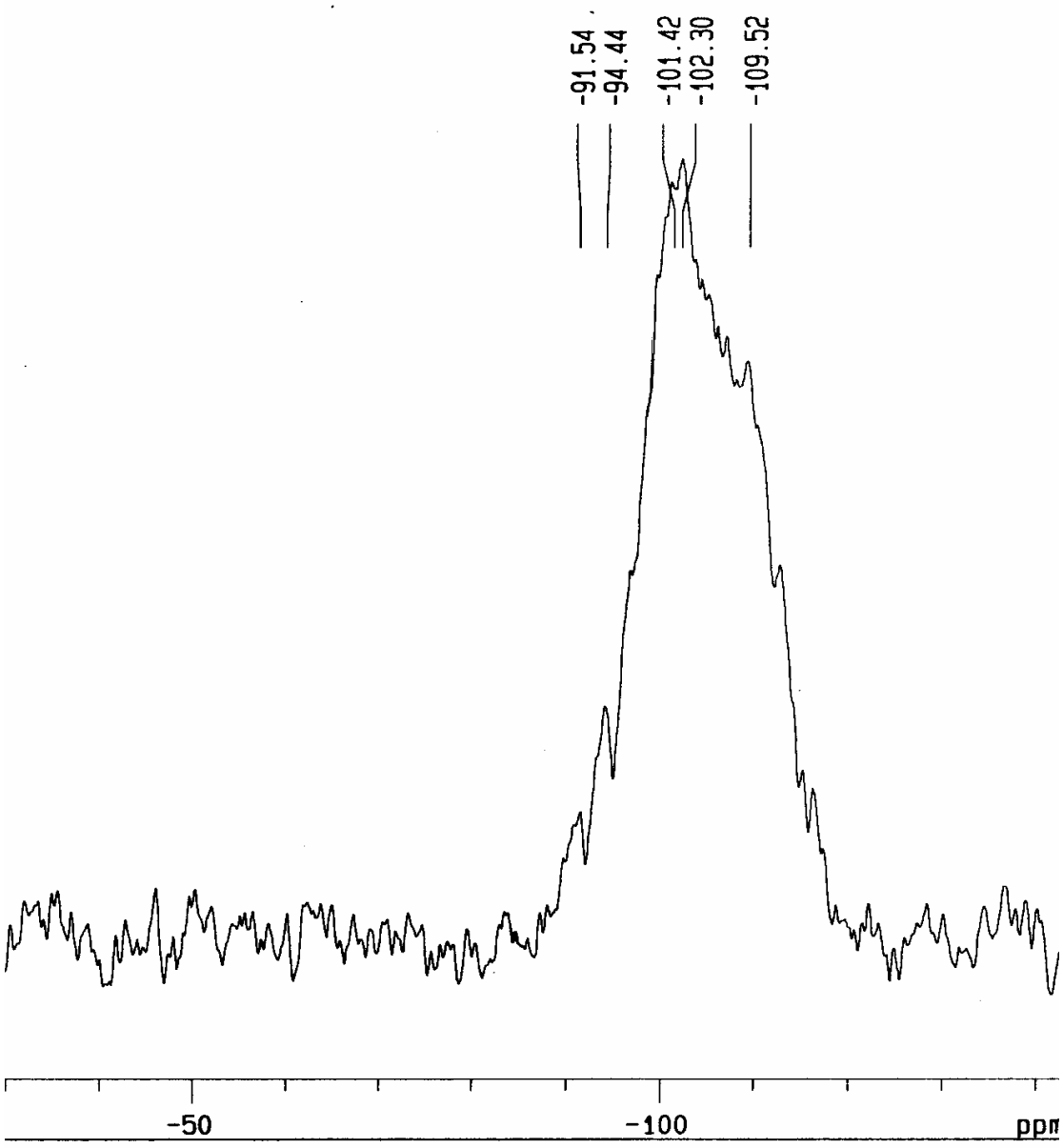


Figure A4.1.

^{29}Si CP MAS Rh15W10MCM-E

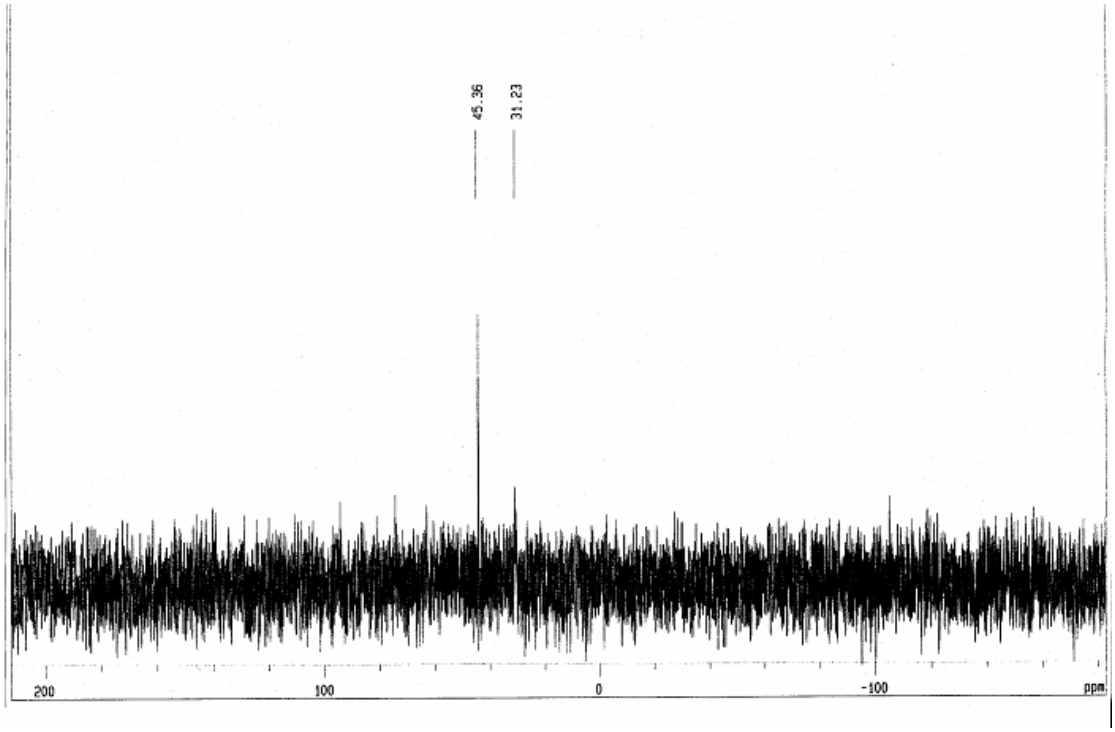
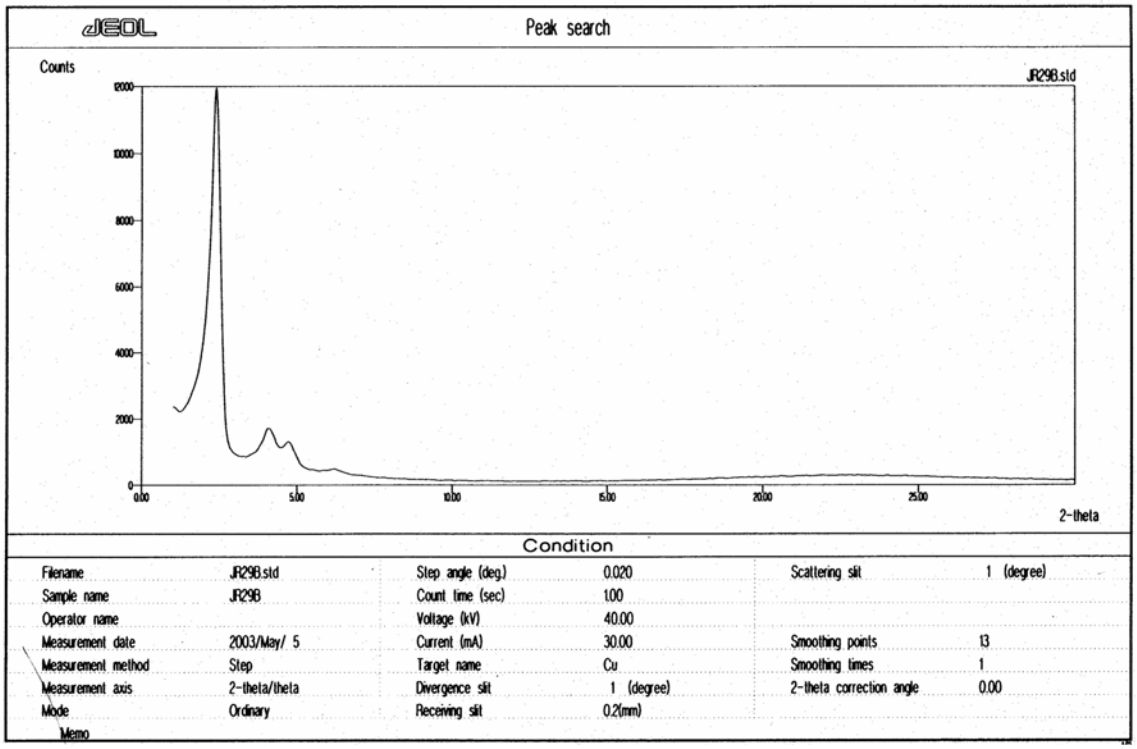


Figure A4.2.

^{31}P CP-MAS NMR OF Rh15W10MCM-E



Condition

Filename	JR29B.std	Step angle (deg.)	0.020	Scattering slit	1 (degree)
Sample name	JR29B	Count time (sec)	1.00		
Operator name		Voltage (kV)	40.00		
Measurement date	2003/May/ 5	Current (mA)	30.00	Smoothing points	13
Measurement method	Step	Target name	Cu	Smoothing times	1
Measurement axis	2-theta/theta	Divergence slit	1 (degree)	2-theta correction angle	0.00
Mode	Ordinary	Receiving slit	0.2(mm)		
Memo					

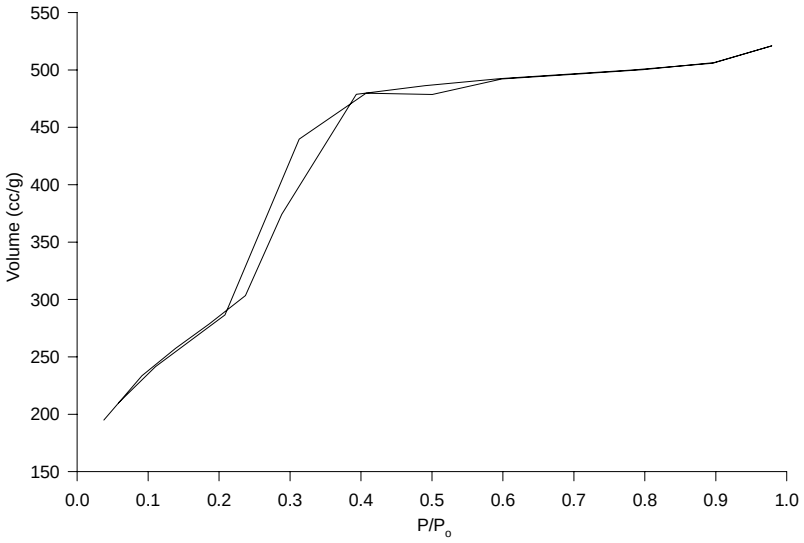


Figure A4.4. Nitrogen sorption isotherm of MCM-41 (30 Å)

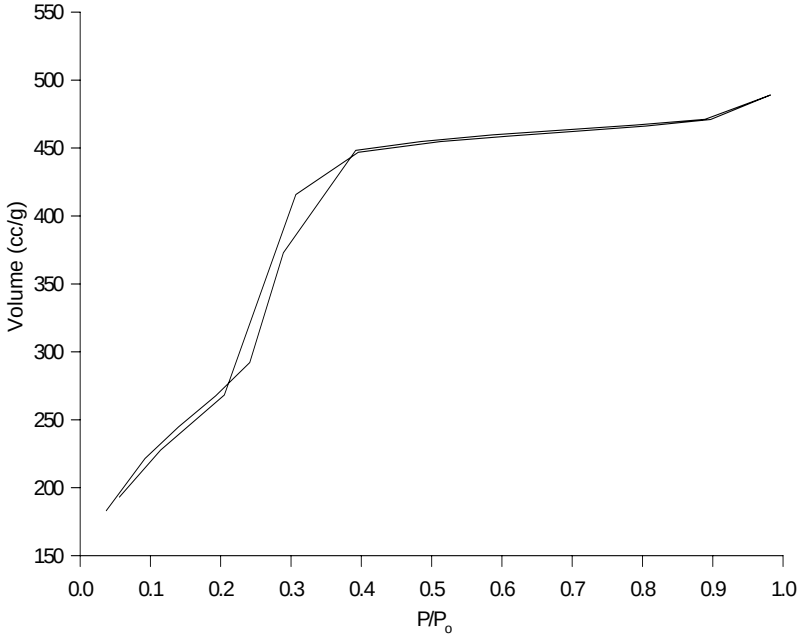


Figure A4.5. Nitrogen sorption isotherm of the catalysts **Rh*3*2W10MCM-*M*** [MCM = MCM-41 (30 Å)]

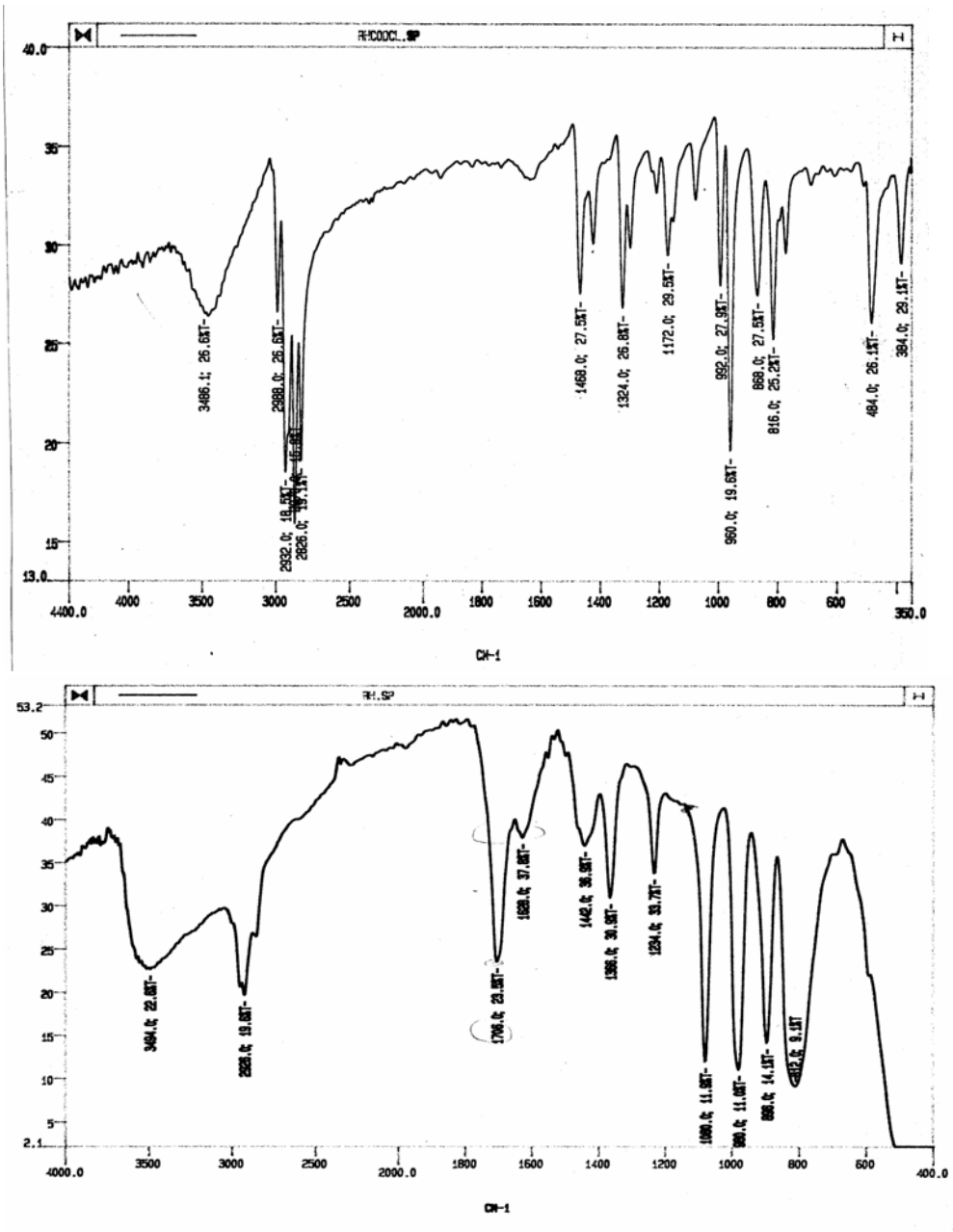


Figure A4.7a **IR** Spectra of the pure commercial complex $[Rh(COD)Cl]_2$ (upper spectra);
Figure A4.7b **IR** Spectra of the pure commercial complex **HPA-W_{12}** (lower spectra).

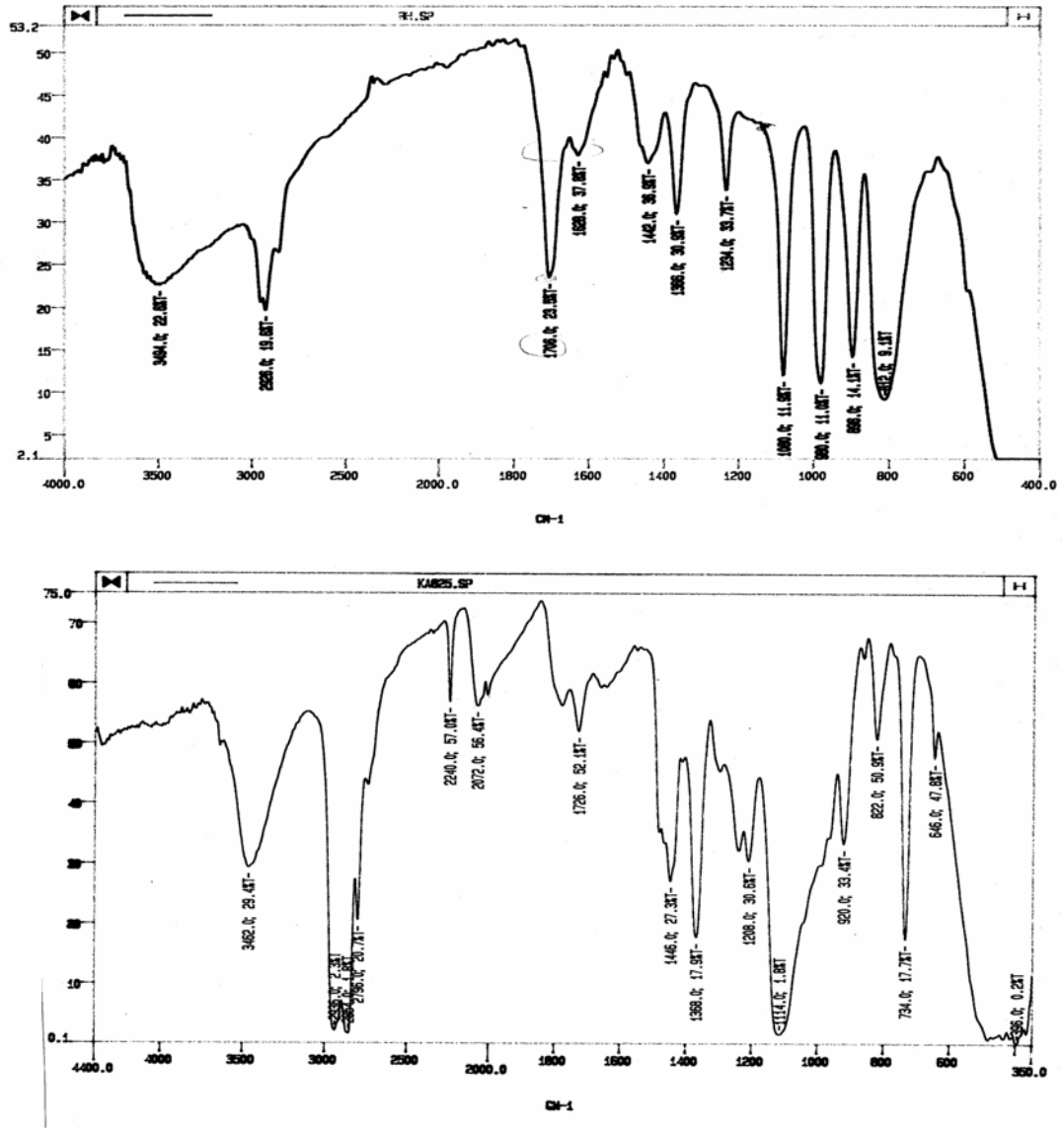


Figure A4.8a. IR Spectra of the solid obtained from the reaction of $[Rh(COD)Cl]_2$ and HPA-W_{12} in methanol for 20 h at room temperature (upper spectra); Figure A4.8b IR Spectra of the solid obtained from the treatment of $[Rh(COD)Cl]_2$ and HPA-W_{12} in THF under CO/H_2 at 80^oC for16h (lower spectra).

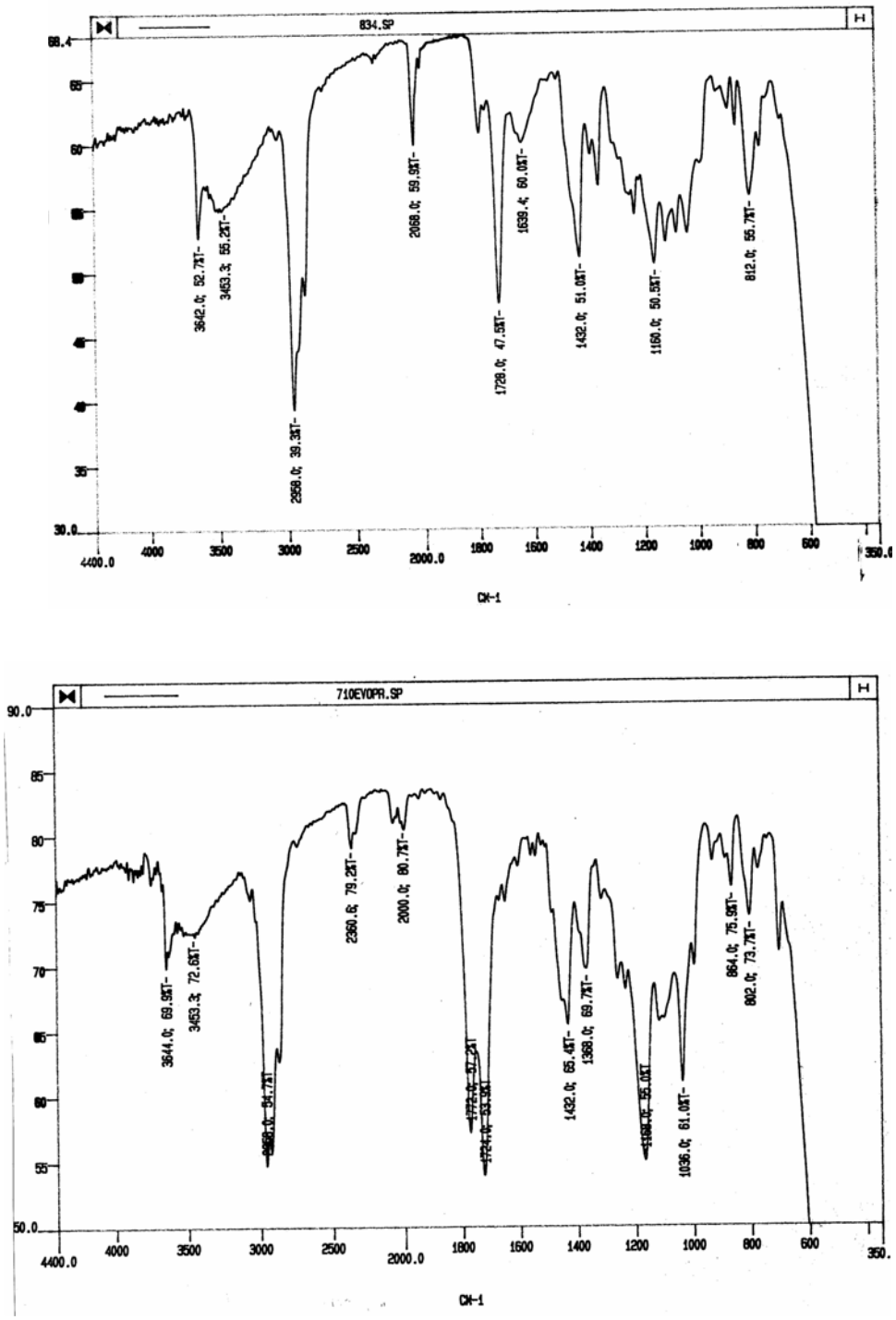


Figure A4.8c. IR Spectra of the solid obtained from the liquid phase after the treatment of $Rh^{A}12MCM\text{-}M$ in THF under CO/H_2 at 80 ^{o}C for16h (upper spectra); Figure A4.8d. IR Spectra of the solid obtained from the liquid phase after the treatment of $Rh^{A}12W10MCM\text{-}M$ in THF under CO/H_2 at 80 ^{o}C for16h (lower spectra).

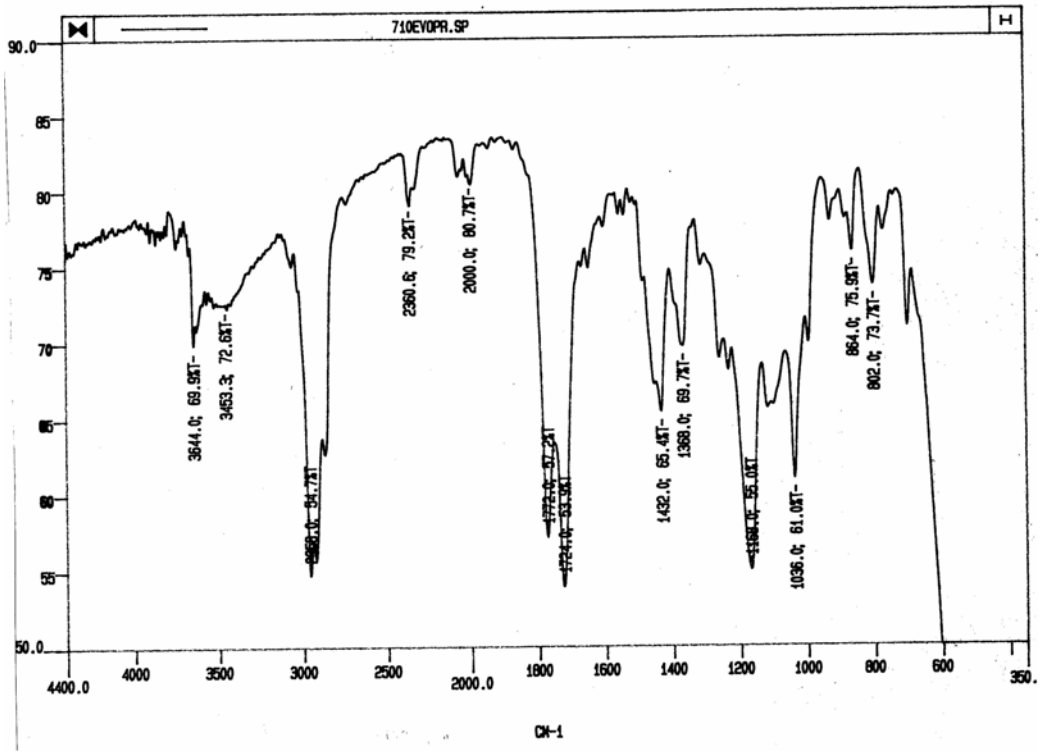


Figure A4.8e IR Spectra of the solid obtained from the liquid phase after the treatment of $Rh^{A}12W10MCM\text{-}M$ in THF under CO/H_2 at 80 ^{o}C for16h.

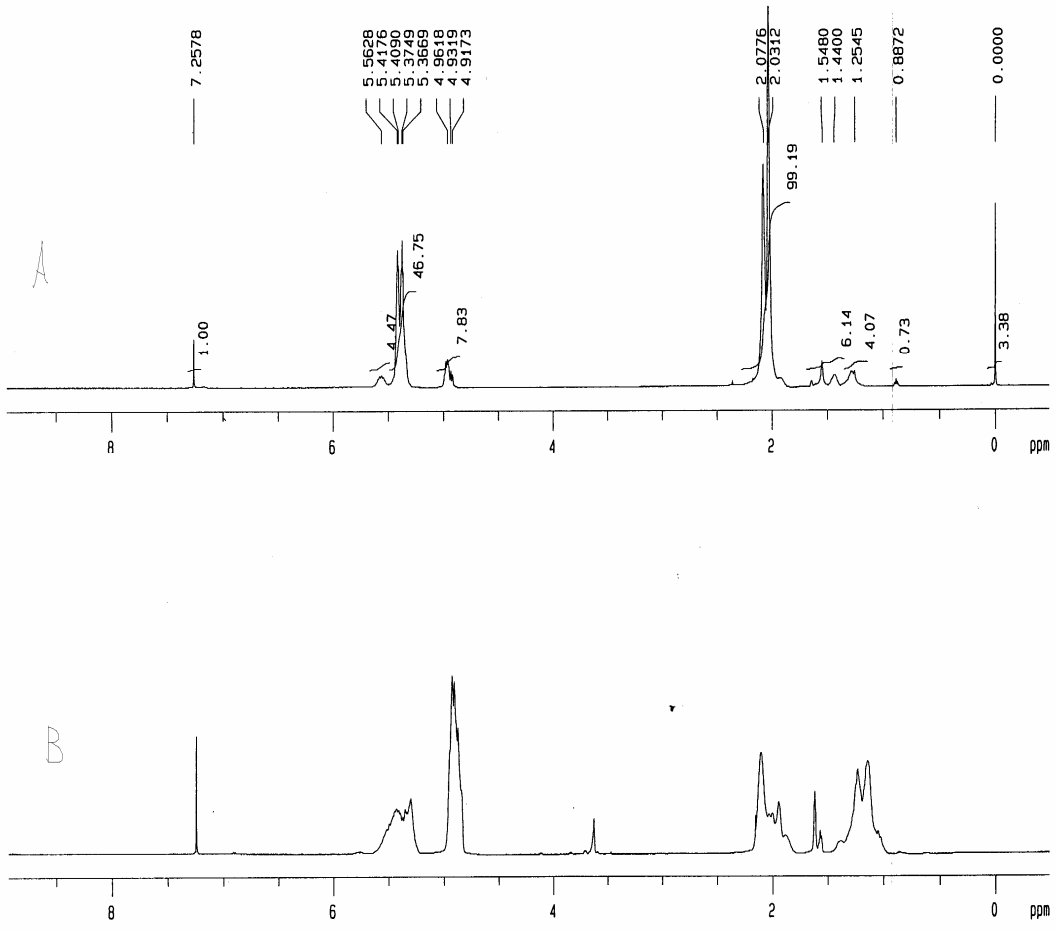


Figure A6.1

A) ^{1}H NMR **PDB86%1,2Pred** and B) ^{1}H NMR **PBD72%1,4Pred**

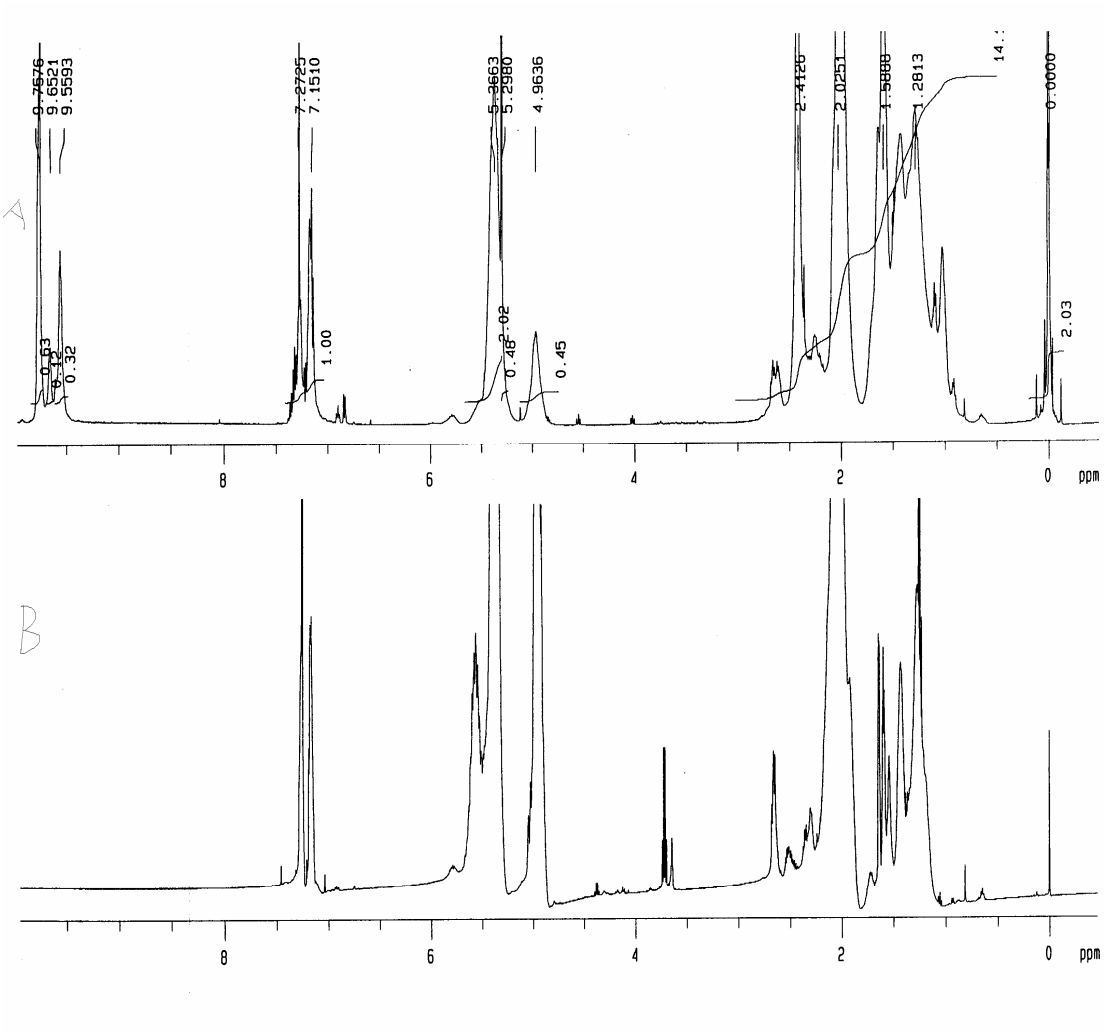


Figure A6.2

a) ^{1}H NMR of Partially hydroformylated **PBD99%Ph**

b) ^{1}H NMR of **PBD99%Ph**

Abbreviations

Ar aromatic

atm atmosphere

B branched

binap 2,2’-bis(diphenylphosphino)-1,1’-binaphthyl

br broad

Cat catalyst

COD 1,5-cyclooctadiene

d doublet

dba dibenzylidene acetone

DIOP 2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

DME dimethyl ether

dppb 1,4-bis(diphenylphosphino)butane

dppe 1,2-bis(diphenylphosphino)ethane

dppp 1,3-bis(diphenylphosphino)propane

dpppt 1,5- bis(diphenylphosphino)pentane

dppm bis(diphenylphosphino)methane

DMA dimethyl acetamide

DMF dimethyl formamide

DMSO dimethyl sulfozide

Et ethyl

eq equation

FT fourier transform

GC Gas chromatography

GC-MS Gas chromatography mass spectroscopy

h hour

i iso

Hz hertz, cycle per seconds

IR infrared

J coupling constant, in Hz

L linear

m multiplet

n normal

MCM-41 Mobil Catalytic Material # 41

Me methyl

med medium

NMR nuclear magnetic resonance

OAc^- acetate ion

PBD Polybutadiene

P_{co} carbon monoxide pressure

Pd Palladium

Ph phenyl

P_{H2} hydrogen pressure

PPh_3 triphenylphosphine

ppm part per million

psi per square inch

PTC Phase transfer catalysis

q quartet

Rh Rhodium

r.t room temperature

s singlet

sh sharp

t triplet

THF Tetrahydrofuran

TRPTC Thermoregulated phase transfer catalysis

TRPSC Thermoregulated phase-separable catalysis

TMBC Thermomorphic biphasic catalysis

TPPTS Triphenylphosphine trisulfonate

TMS **tetramethylsilane**

δ chemical shift

Vita

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